J. Applied Membrane Science & Technology, Vol. 29, No. 1, April 2025, 41-53

Modification of PVDF Hollow Fiber Membranes by SMM Coating for Pharmaceutical Wastewater Treatment through a Liquid-Liquid Membrane Contactor System

Ismail Afshari[a] & Amir Mansourizadeh[a,b*]

[a]Department of Chemical Engineering, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran
[b]Department of Civil Engineering, Apadana Institute of Higher Education, 7187985443 Shiraz, Iran

Submitted: 23/11/2024. Revised edition: 26/12/2024. Accepted: 6/1/2025. Available online: 27/3/2025

ABSTRACT

Given the potential environmental and health hazards posed by pharmaceutical wastewater, effective treatment methods are crucial. A liquid-liquid membrane contactor is an innovative separation technology applied in wastewater treatment. This study involved the fabrication and modification of highly porous polyvinylidene fluoride (PVDF) hollow fiber membranes with a surface-modifying macromolecule (SMM) coating for the extraction of penicillin-G from wastewater using a liquid-liquid membrane contactor system. FESEM analysis demonstrated a thin outer layer characterized by a finger-like structure, along with a thick sub-layer exhibiting sponge-like properties in the membrane. The decrease in inner surface porosity and pore size indicated the development of a thin SMM-coated layer. The modified membrane displayed an overall porosity of around 80%. The water contact angle on the inner surface increased from approximately 87° to 108° after SMM coating, indicating improved surface hydrophobicity. Additionally, the liquid entry pressure of the modified PVDF membrane rose from 450 to 550 kPa. The modified membrane featured an average pore size of 0.22 μm and an effective surface porosity of 2180 m^{-1}, signifying considerable permeability. Over 30 hours of operation in the membrane contactor, the modified membrane maintained a consistent penicillin-G extraction flux of 1.18×10^{-3} kg/m^2 s, while the unmodified PVDF membrane experienced a 32% decrease in flux. Thus, the enhanced PVDF hollow fiber membrane, with its improved surface hydrophobicity and permeability, shows great potential for wastewater treatment utilizing a liquid-liquid membrane contactor process.

Keywords: Porous PVDF membrane, SMM coating, Penicillin-G extraction, Liquid-liquid membrane contactor, Pharmaceutical wastewater treatment

1.0 INTRODUCTION

Pharmaceutical wastewater can be originated from various sources, including manufacturing facilities, hospitals and healthcare facilities, and animal farms [1]. This type of wastewater can contain a variety of contaminants, including active pharmaceutical ingredients (APIs), solvents, heavy metals, and other hazardous substances. Due to the potential environmental and health risks associated with these pollutants, proper treatment and management of pharmaceutical wastewater are essential. Effective treatment methods may include physical, chemical, and biological processes designed to remove or neutralize harmful components before the wastewater is discharged into the environment [2]. Regulatory frameworks often govern the handling and disposal of pharmaceutical

* Corresponding to: Amir Mansourizadeh (email: a.mansourizadeh@yahoo.com)
DOI: https://doi.org/10.11113/jamst.v29n1.309

wastewater to ensure compliance with environmental standards and protect public health.

Membrane separation processes play a crucial role in the treatment of pharmaceutical wastewater, offering effective separation and purification processes. The choice of membrane technology depends on factors such as the specific contaminants present, desired effluent quality, operational costs, and regulatory requirements. Proper selection and optimization of membrane processes can significantly improve the sustainability and environmental impact of pharmaceutical disposal practice. A liquid-liquid membrane contactor is an advanced separation technology used in wastewater treatment, particularly for the removal of specific contaminants, such as organic solvents, heavy metals, and other hazardous substances [3]. This technology utilizes a semi-permeable membrane to facilitate mass transfer between two immiscible liquid phases without allowing them to mix directly. Two immiscible liquids are used in a liquid-liquid membrane contactor including the feed phase (containing the contaminants) and the stripping phase (extracting the contaminants). The two phases are separated by a porous membrane. The membrane allows for the selective transfer of specific solutes from the feed phase to the stripping phase while preventing the bulk flow of liquids. Atsbha *et al*. [4] applied lab scale and pilot scale hollow fiber membrane contactors for recovering ammonia from pharmaceutical wastewater. The H_2SO_4 solution of 5% was used as the stripping solution. For ammonia feed concentrations in the range of 600–6000 mgNH_4^+-N/L, the removal efficiency from a real wastewater was stable for three cycles. Abbasisoraki *et al*. [5] fabricated advanced poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) hollow fiber membranes for extracting penicillin-G from the wastewater in a liquid-liquid membrane contactor operation. The stripping phase was organic solution of Aliquat 336 (5 wt.%). At optimum operating conditions, a maximum extraction flux of 1.55×10^{-3} kg/m^2 s was achieved. In another study, the effectiveness of PVDF-HFP and polysulfone (PSF) hollow fiber membrane contactors in separating antibiotics from pharmaceutical wastewater was compared [6]. The PVDF-HFP membrane presented a higher extraction flux than the PSF membrane in separating penicillin-G from wastewater owing to the enhanced porosity and hydrophobicity. Modeling and simulation of removing ibuprofen from pharmaceutical wastewater through a hollow fiber membrane contactor were performed by Deriss *et al*. [7]. It was found that the enhancement of the removal efficiency was affected by the membrane porosity and the length of hollow fibers. Additionally, the ibuprofen removal efficiency was improved to 93.2% by increasing the inner radius and the number of fibers in the membrane module.

While membrane contactors offer several advantages for wastewater treatment, they also face a number of challenges and problems that can affect their performance and efficiency [8]. In this context, the key issues include membrane fouling and membrane wetting. Membrane fouling occurs when contaminants accumulate on the membrane surface or within its pores. This can lead to reduced permeability, increased resistance to mass transfer, and ultimately decreased efficiency of the separation process. Fouling can be caused by organic matter, suspended solids, colloids, and biofilms. Membrane wetting occurs when the feed phase penetrates into the membrane pores, leading to a loss of selectivity and

performance. Total wetting can compromise the separation process by allowing direct mixing of the two liquid phases, which defeats the purpose of using a membrane.

Hydrophobic surface modification can be a successful method for reducing membrane wetting in liquid-liquid membrane contactors. This modification can be achieved using several techniques, including grafting, coating, and blending [9]. Coating, which is a straightforward and effective method, has been widely utilized for different applications due to the advantage of easily adjusting the thickness of the coating layer. Applying a hydrophobic ultra-thin coating layer can help decrease the membrane's wetting resistance. Surface-modifying macromolecules (SMMs) are valuable materials for enhancing the performance of membranes by improving their resistance to wetting and fouling [10]. It should be noted that most of the former studies have focused on SMM blending for polymeric membrane fabrication, where incomplete movement of SMM to the membrane surface could not extensively improve the hydrophobicity [11–13]. Mansourizadeh *et al*. [11] developed a blend of PVDF and SMM to create hollow fiber membranes specifically designed for CO_2 absorption using a membrane contactor system. Their findings indicated that incorporating 2 wt.% SMM led to an increase in pore sizes and enhanced surface hydrophobicity. As a result, the membranes achieved a stable CO_2 flux of approximately 3.3×10^{-4} mol/m²·s over a continuous operation period of 130 hours. In a different investigation, Shoaie *et al*. [14] focused on optimizing the surface characteristics of PVDF membranes for membrane distillation applications by integrating SMM into the casting solution. The optimized PVDF/SMM membrane exhibited a water contact angle of 108°, indicating significant hydrophobicity. Moreover, it achieved impressive performance, including a maximum water flux of 17.5 kg/m²·h and a salt rejection rate of 99.9%.

In this study, a novel approach was taken by applying an ultra-thin layer of SMM onto the inner surface of porous PVDF hollow fiber membranes to extract penicillin-G from a simulated wastewater. The membranes were produced using a dry-wet spinning technique. Various tests, such as N_2 permeation, SEM analysis, water contact angle (WCA) measurement, liquid entry pressure (LEP) assessment, and overall porosity evaluation, were conducted to analyze the structural characteristics of both the uncoated and coated membranes. Furthermore, a liquid-liquid membrane contactor system was employed to evaluate the long-term extraction efficiency of the membranes.

2.0 METHODS

2.1 Materials

Commercial PVDF pellets (Kynar® 740) were provided by Arkema and used for hollow fiber membrane fabrication. NMP (>99.5%, Merck, Germany) served as the polymer solvent for producing the PVDF solution. To enhance membrane porosity, ortho-phosphoric acid (PA) (85%, Merck, Germany) was added as a non-solvent additive during solution preparation. The hydrophobic SMM was provided by the department of chemical and biological engineering at the University of Ottawa. The details of SMM synthesis procedure can be found elsewhere [15]. Tetrahydrofuran (THF) (≥99.9%, Sigma-Aldrich) was utilized to prepare the SMM coating solution. Potassium salt of penicillin-G (MW= 372.48 g/mol) was provided by Sigma-Aldrich to prepare the simulated wastewater.

Sodium acetate and glacial acetic acid were purchased from Merck and used for buffer preparation. Aliquat 336 (Sigma-Aldrich) acted as the carrier, and oleyl alcohol (85%, Merck) served as the solvent for the stripping solution. Distilled water was used where it was required.

2.2 PVDF hollow fiber membrane fabrication and surface coating by SMM

Based on our previous studies, the composition of the polymer solution was fixed to achieve a highly porous structure [16, 17]. The solution was prepared by mixing 3 wt% PA in NMP, then slowly incorporating 16 wt% PVDF (under continuous stirring at 60 °C). The hollow fiber membranes were subsequently produced through a dry-wet spinning technique, with pre-established spinning parameters to achieve the intended porous structure, as described in another source [18]. After fabrication, the membranes underwent a 3-day immersion in distilled water to eliminate residual solvent and non-solvent. Subsequently, they were soaked in pure ethanol for 15 minutes to reduce shrinkage before being dried at room temperature.

To improve the resistance to wetting and durability of PVDF membranes used for extracting penicillin-G in membrane contactor operations, an ultra-thin layer of SMM was applied to the inner surface of the hollow fibers. The SMM coating solution was prepared by dissolving 5 wt% SMM in THF with continuous stirring at room temperature, followed by filtration using a 20 μm stainless steel mesh. Subsequently, the coating solution was allowed to flow through the lumen side of the hollow fibers under the influence of gravity for a period of 30 seconds. Any excess coating solution remaining in the hollow fibers' lumen was eliminated by blowing nitrogen. To cure the coated hollow fibers, they were placed in a vacuum oven at 70 °C for 12 hours.

2.3 Characterization of hollow fiber membranes

Field emission scanning electron microscopy (FESEM) (ZEIZZ SUPRA 35VP) was applied to analyze the cross-section, outer surface and inner surface morphology of the hollow fiber membranes.

To evaluate wetting stability of the prepared hollow fiber membranes, liquid entry pressure (LEP) and contact angle tests were performed. For LEP test, distilled water was pressurized in the lumen side of the membranes by using a diaphragm pump, where the pressure was improved step by step at 50 kPa intervals. The hollow fibers were reserved under constant pressure for 10 min for checking the appearance of first droplet on the outer surface, which this pressure is known as CEPw. For contact angle measurement of the dried membranes, a goniometer (DSA20E, KRUSS) was used. The contact angle of ten different places on the inner surface of the membranes was measured, then an average value was reported.

Overall porosity of the membranes was estimated based on density measurement. The dried membrane samples were weighted to measure the hollow fibers density. The overall porosity (ε_o) is given as [5]:

$$\varepsilon_o(\%) = \left(1 - \frac{\rho_f}{\rho_p}\right) \times 100 \qquad (1)$$

where the polymer and hollow fiber density are known as ρ_p and ρ_f (g/ cm^3), respectively. ρ_p for PVDF is 1.78 g/cm^3. The density of hollow fibers is calculated as:

$$\rho_f = \frac{4w}{\pi(d_o^2 - d_i^2)L} \qquad (2)$$

where the length, inner and outer diameter of the hollow fibers are L, d_i and d_o (cm), respectively. W is mass of the hollow fibers (g).

The N_2 permeation experiment was applied to assess mean pore size and effective surface porosity of the membranes. The procedure for measuring the gas permeation rate was given, elsewhere [18]. By assuming the straight and cylindrical pores on the outer skin layer of the membrane, Poiseuille and Knudsen flows in a parallel connection can be considered to measure N_2 permeance (J_{N2}) [19, 20]:

$$J_{N2} = \frac{2r_p\varepsilon_s}{3RTL_p}\left(\frac{8RT}{\pi M}\right)^{0.5} + \frac{r_p^2}{8\mu RT}\frac{\varepsilon_s}{L_p}\bar{P} \quad \text{or} \quad J_{N2} = K_0 + P_0\bar{P} \tag{3}$$

where L_p and r_p are pore length and radius (m), respectively; ε_s is surface porosity (-); R is universal gas constant 8.314 (J/mol.K); μ is N_2 viscosity (kg/m.s); M is N_2 molecular weight (kg/mol); T is gas temperature (K); and $\bar{P}$ is mean pressure (Pa). After plotting J_{N2} vs. $\bar{P}$, the intercept (K_0) and slope (P_0) of the permeance line were found to estimate mean pore size (r_p) and surface porosity over pore length (ε/L_p) as:

$$r_p = 5.33\left(\frac{P_0}{K_0}\right)\left(\frac{8RT}{\pi\mu}\right)^{0.5}\mu \tag{4}$$

$$\frac{\varepsilon}{L_p} = \frac{8\mu RTP_0}{r_p^2} \tag{5}$$

2.4 Extraction of Penicillin-G through Liquid-liquid Membrane Contactor System

Extraction of penicillin-G was conducted through a liquid–liquid membrane contactor system to assess penicillin-G flux. For preparation of the membrane module, 20 hollow fibers were randomly packed in a stainless steel tube, as the properties shown in Table 1. The representation of the experimental liquid–liquid membrane contactor system is given in Figure 1. A continuous counter-current mode of operation was set for the wastewater feed and the stripping phase in the membrane contactor system.

Table 1 Properties of the membrane contactor module

Parameter (unit)	Value
Module inner diameter (cm)	1.4
Module length (cm)	30
Effective fibers length (cm)	20
Fiber outer diameter (cm)	0.095
Fiber inner diameter (cm)	0.055
Number of fibers (–)	20
Membrane area (cm^2)	119.3

The simulated wastewater with concentration of 250 mg/L was prepared by dissolving potassium salt of penicillin-G in the buffer of acetic acid and its salt with pH of 4.5. In order to prepare the organic stripping solution, 5 wt% of Aliquat 336 was dissolved in the required amount of oleyl alcohol. Using a diaphragm pump, the wastewater feed was flowed from the tank into the lumen side of the hollow fibers and its flowrate was set in 100 mL/min. The stripping solution was flowed from the tank into the module shell side and its flowrate was also set in the 100 mL/min. The stripping phase pressure was set on 100 kPa using the by-pass valve of the pump. The wastewater pressure was controlled 50 kPa higher than the stripping phase to prevent the leakage of the stripping solution into the wastewater. The operation was conducted at room temperature (around 26 °C) because our previous research indicated that the

extraction flux of penicillin-G increased as the temperature rose from 8 °C to approximately 30 °C [5]. Using a UV–Vis spectrophotometer (PerkinElmer) at a maximum wavelength of 235 nm, the concentration of the wastewater at outlet of the module was measured to calculate the extraction flux. The UV calibration curve was attained at five standard concentrations of penicillin-G. The wastewater samples were taken at outlet of the module during the experiments. The penicillin-G extraction flux (J_E) was calculated by the following equation:

$$J_E = \frac{Q_w \times (C_{in} - C_{out})}{A_i} \quad (6)$$

where Q_w is the wastewater flowrate (m^3/s), A_i is the inner surface area of the membranes (m^2) and C_{in} and C_{out} are the penicillin-G concentrations (kg/m^3) in the feed and outlet of the module, respectively

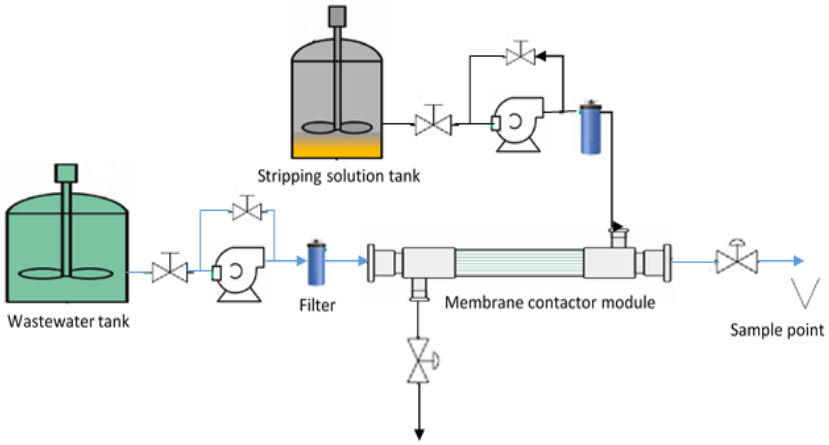

Figure 1 Schematic of the experimental liquid–liquid membrane contactor system

3.0 RESULTS AND DISCUSSION

3.1 Morphology of the PVDF hollow fiber membranes

It is worth mentioning that the permeability and surface hydrophobicity are the main factors for membrane contactor applications. Firstly, an attempt was made to fabricate porous PVDF hollow fiber membranes with high gas permeability. Secondly, the inner surface was coated by a thin layer of SMM to enhance hydrophobicity with minimum effect on the permeability drop. For improving permeability, the polymer dope composition was set close to the cloud point by addition of 3% PA. The FESEM images of cross section, outer surface and inner surface morphology of the prepared PVDF membranes are shown in Figure 2. The hollow fiber membranes presented inner diameter, outer diameter and wall thickness of around 550 µm, 950 µm and 200 µm, respectively. As can be seen, an outer finger-like layer with thickness of about 50 µm and a sponge-like sub-layer with thickness of about 150 µm were formed. The formation of finger-like layer can be correlated to the fast solidification at initial stage of phase separation owing to the addition of PA which could increase thermodynamic instability of the solution [21]. On the other hand, the sponge-like layer formation can be related to the kinetic effect of the solution viscosity and also using a weak non-solvent as the bore fluid which resulted in a delay phase separation [22]. The PVDF membrane demonstrated an inner skin-less microporous structure because of applying a weak non-solvent of 80/20 NMP/water as the bore fluid. There

were insignificant deviations in the cross-section and outer surface morphology of the membranes after SMM coating. However, the inner surface morphology was considerably affected by SMM coating. The ultra-thin SMM coated layer with thickness of around 0.2 µm can be seen in Figure 2F. The pore sizes on the inner surface diminished, with some pores becoming blocked by the SMM coated layer. While the SMM coating may reduce the membrane's surface porosity and permeability to some extent, the increased surface hydrophobicity could improve separation performance. This effect will be discussed further in the subsequent sections.

3.2 Properties of the PVDF hollow fiber membranes

The structure of the pristine and SMM coated membranes were examined by various tests and the results are given in Table 2. The pristine membrane showed a significant porosity of approximately 80% which is in accordance with the FESEM images. Following the application of the SMM coating, there was a slight decrease in overall porosity. This decrease is likely due to the coating solution penetrating the membrane matrix, resulting in a minor reduction in void fraction. It can be said that the high porosity of the prepared membrane is beneficial for penicillin-G extraction as it offers low mass transfer resistance.

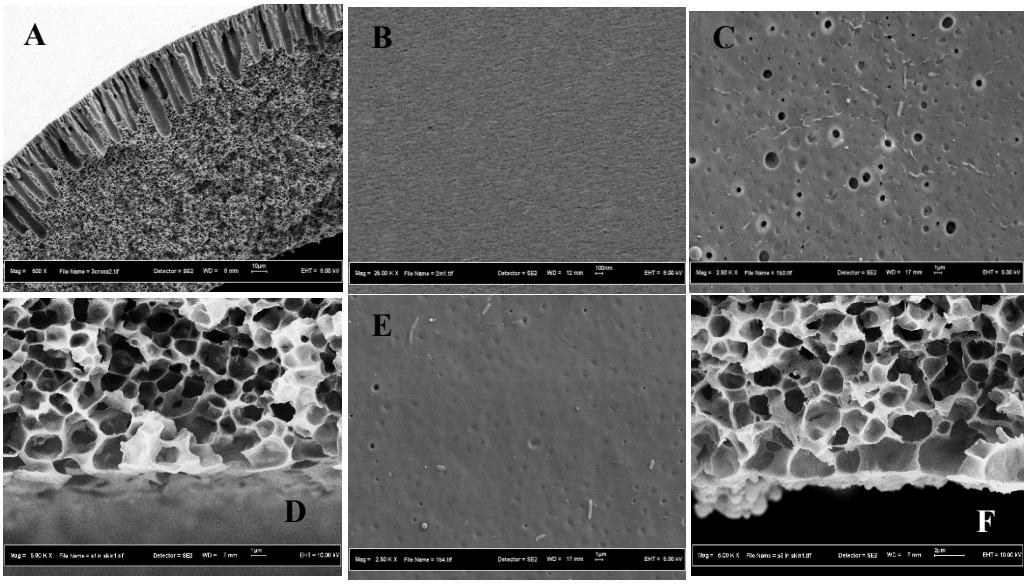

Figure 2 FESEM images of the PVDF hollow fiber membranes: (A) cross section; (B) outer surface; (C) inner surface; (D) inner surface cross section; (E) inner surface after SMM coating; and (F) inner cross section after SMM coating

Table 2 Properties of the PVDF hollow fiber membranes

Characteristic (unit)	PVDF	PVDF-SMM
N_2 permeance @ 100 kPa (cm^3/cm^2 s cmHg)	0.019	0.016
Mean pore size (µm)	0.36	0.22
Effective surface porosity (m^{-1})	2790	2180
Overall porosity (%)	80.2	79.5
LEP (kPa)	450	550
Outer surface WCA (°)	88.2±1.09	89.4±1.45
Inner surface WCA (°)	86.8±1.16	108.3±2.18

The wetting resistance of the PVDF hollow fiber membranes was estimated by LEP and WCA experiments. Although there was insignificant changes in outer surface WCA, the inner surface WCA of the SMM coated increased from around 87° to 108° which confirmed the improved surface hydrophobicity. Additionally, the LEP of the membrane increased from 450 to 550 kPa after SMM coating which can be related to the enhanced surface hydrophobicity and the reduced pore sizes. It is worth mentioning that wetting resistance of the porous membranes is connected to the surface hydrophobicity, pore size and liquid surface tension according to Laplace-Young equation [23].

The mean pore size and effective surface porosity of the pristine and SMM coated PVDF membranes were estimated by N_2 permeation test and the results are given in Table 2. The membrane's mean pore size and surface porosity decreased after the SMM coating. In addition, the N_2 permeance slightly decreased from 0.019 to 0.016 cm^3/cm^2 s cmHg, which can confirm the formation of an ultra-thin coated layer. The mean pore size of 0.22 µm and effective surface porosity of 2180 m^{-1} were found for the SMM coated membrane. Consequently, the enhanced PVDF-SMM membrane with improved permeation and increased hydrophobicity is anticipated to enhance penicillin-G extraction in the liquid-liquid membrane contactor process. Figure 3 shows N_2 permeance of the PVDF hollow fiber membranes as a function of mean pressure. The intercept and slope of the N_2 permeance lines can be used to calculate pore size and surface porosity by Eqs. (4) and (5). The slop of the line for the pristine membrane is higher than the SMM coated membrane. This means that the Knudsen flow was overtaken by the Poiseuille flow which confirmed the larger pore sizes of the pristine membrane.

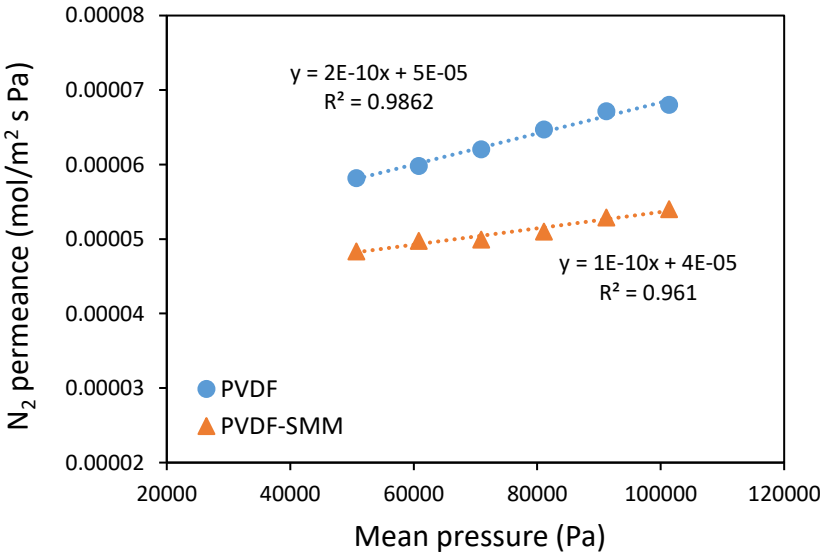

Figure 3 N_2 permeance of the PVDF hollow fiber membranes

3.3 Performance of the PVDF Hollow Fiber Membranes for Penicillin-G Extraction

When operating at a flow rate of 100 mL/min for both the feed and stripping solutions, a temperature of 26 °C, and an operating pressure of 100 kPa, the penicillin-G extraction flux of the membranes was monitored over time, as depicted in Figure 4. The pristine membrane experienced a notable

decline in flux from 1.45×10^{-3} to 9.8×10^{-4} kg/m^2 s over 30 hours of membrane contactor operation. This decline can be attributed to membrane wetting, particularly evident in the initial 15 hours of operation. Since the pristine PVDF membrane showed larger pore sizes and lower surface hydrophobicity, it is more prone to pore wetting compared to the PVDF-SMM membrane. A similar trend of flux reduction over time was reported for the pristine poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) membrane contactor during phenol extraction [24]. In contrast, the SMM coated membrane showed only a 13% reduction in flux over the same 30-hour period, maintaining a relatively stable penicillin-G extraction flux of about 1.18×10^{-3} kg/m^2 s. This improved performance is likely due to the enhanced structure with smaller pore sizes and increased surface hydrophobicity, which enhances wetting resistance. This is supported by the Laplace-Young equation [23], which indicates that wetting pressure of a porous membrane is directly related to the contact angle and inversely related to the pore size.

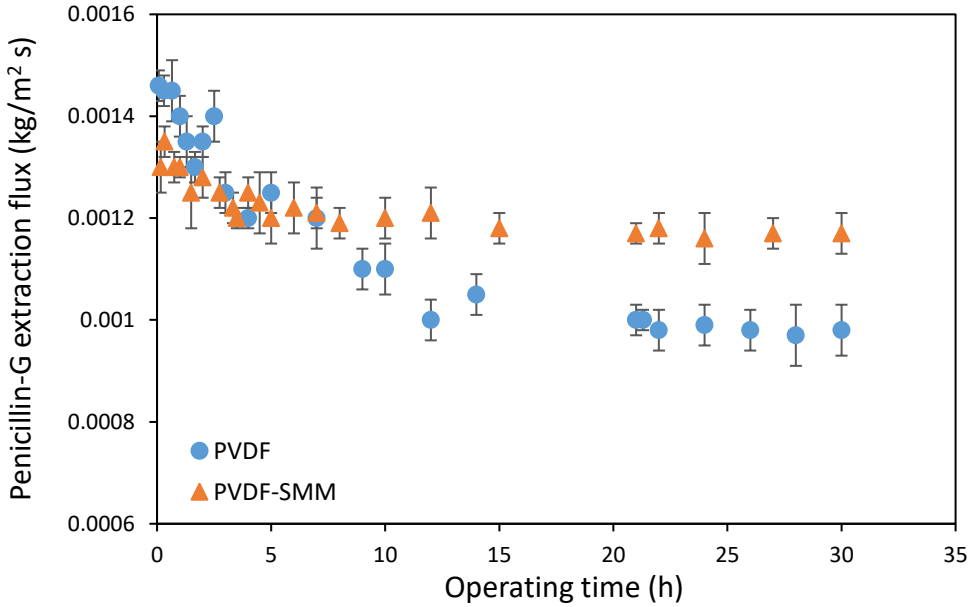

Figure 4 Penicillin-G extraction flux of the PVDF hollow fiber membranes

Table 3 compares the penicillin-G extraction flux of various hollow fiber membrane contactors. The enhanced PVDF-SMM membrane exhibited significantly higher extraction flux compared to the commercial polypropylene (PP) membranes. PP membranes, typically produced through thermal and stretching methods, have a symmetric structure with lower porosity than membranes made through the phase-inversion process. Despite good hydrophobicity, the low porosity and permeability of PP membranes appear to limit extraction flux. Furthermore, the asymmetric PVDF-HFP membrane, known for its high hydrophobicity and permeability, showed a moderately higher extraction flux compared to the PVDF membrane developed in this study.

Table 3 Performance comparison of various hollow fiber membrane contactors for penicillin-G extraction

Membrane	Pore size (µm)	Porosity (%)	Operating conditions	Penicillin-G flux (kg/m^2 s)	Ref.
Commercial polypropylene (PP)	-	75	Feed temperature: 22 °C; feed concentration: 50 mmol/L; feed pH= 6; organic phase flow rate: 1.18 L/h; aqueous phase flow rate:2.7 L/h; organic phase concentration:7% di-n-octylamine.	1.6×10^{-4}	[25]
Commercial PP (Celgard X-30)	0.08×0.23	45	Feed temperature: 25 °C; feed concentration: 20 mmol/L; feed pH= 4.5; aqueous phase flow rate: 3.6–4.4 L/h; organic phase flow rate: 3.3–3.6 L/h; organic phase concentration: 253 mmol/L Amberlite LA-2.	5.9×10^{-6}	[26]
In-house made PVDF-HFP	0.038	84	Feed temperature: 41 °C; feed concentration: 218 mg/L; feed pH= 4.5–5; aqueous phase flow rate: 3 L/h; organic phase flow rate: 8.6 L/h; organic phase concentration: 5% Aliquat 336.	1.5×10^{-3}	[5]
PVDF-SMM (present work)	0.22	79	Feed temperature: 25 °C; feed concentration: 250 mg/L; feed pH= 4.5; aqueous phase flow rate: 6 L/h; organic phase flow rate: 6 L/h; organic phase concentration: 5% Aliquat 336.	1.18×10^{-3}	-

4.0 CONCLUSIONS

This study aimed to improve the hydrophobic properties of the inner surface of porous PVDF hollow fiber membranes to maintain a consistent penicillin-G extraction flux during liquid-liquid membrane contactor operations. A thin layer of hydrophobic SMM was applied to the inner surface of the hollow fibers. The membranes were characterized using different tests, and the findings are summarized below:

- From FESEM, a thin outer layer with finger-like morphology and a thick sub-layer with sponge-like morphology were found for the membrane. The inner surface porosity and pore size decreased after SMM coating.
- From N_2 permeation test, the permeance, surface porosity and mean pore size moderately decreased after SMM coating. The modified PVDF membrane presented mean pore size and effective surface porosity of about 0.22 µm and 2180 m^{-1}, respectively.
- Wetting resistance of the SMM coated membrane significantly increased in terms of WCA and LEP. The modified membrane showed inner surface WCA and LEP of 108° and 550 kPa, respectively.

- Over a 30-hour period of operating the liquid-liquid membrane contactor, the modified PVDF membrane exhibited a nearly constant penicillin-G extraction flux of 1.18×10^{-3} kg/m² s. In contrast, the pristine membrane experienced a reduction in extraction flux of approximately 32%.

The modified PVDF hollow fiber membrane with enhanced hydrophobicity and permeability can be a potential alternative for wastewater treatment through a membrane contactor process

ACKNOWLEDGEMENT

We would like to thank Islamic Azad University of Gachsaran for the helpful support.

CONFLICTS OF INTEREST

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

REFERENCES

[1] X. Shi, K. Y. Leong, H. Y. Ng. (2017). Anaerobic treatment of pharmaceutical wastewater: A critical review. *Bioresour Technol*., *245*, 1238–1244.

[2] J. O. Eniola, R. Kumar, M. A. Barakat, J. Rashid. (2022). A review on conventional and advanced hybrid technologies for pharmaceutical wastewater treatment. *J Clean Prod*., *356*, 131826.

[3] A. Amelio, L. Loise, R. Azhandeh, S. Darvishmanesh, V. Calabró, J. Degrève, P. Luis, B. Van der Bruggen. (2016). Purification of biodiesel using a membrane contactor: Liquid–liquid extraction. *Fuel Process Technol*., *142*, 352–360.

[4] M. W. Atsbha, L. Farkash, G. Bartal, O. Nir. (2023). Extracting liquid fertilizer from ammonia-laden pharmaceutical wastewater using Hollow fiber membrane contactors. *J Clean Prod*., *418*, 138183.

[5] F. Abbasisourki, M. H. Jazebizadeh, A. Mansourizadeh, M. R. Hojjati. (2021). Extraction of penicillin-G from pharmaceutical wastewaters via a developed hydrophobic PVDF-HFP hollow fiber membrane contactor and process optimization. *Environ Technol Innov*., *22*, 101406.

[6] F. Abbasisourki, A. Mansourizadeh, M. H. Jazebizadeh. (2024). Performance comparison of hollow fiber membrane contactors for liquid-liquid extraction of penicillin-G from wastewater. *Environ Water Eng*., *10*(3), 299–316.

[7] A. Q. Deriss, S. Langari, M. Taherian. (2021). Computational fluid dynamics modeling of ibuprofen removal using a hollow fiber membrane contactor. *Environ Prog Sustain Energy*., *40*, e13490.

[8] M. Chadni, M. Moussa, V. Athès, F. Allais, I. Ioannou. (2023). Membrane contactors-assisted liquid-liquid extraction of biomolecules from biorefinery liquid streams: A case study on organic acids. *Sep Purif Technol*., *317*, 123927.

[9] N. A. Ahmad, C. P. Leo, A. L. Ahmad, W. K. W. Ramli. (2015). Membranes with great hydrophobicity: a review on preparation and characterization. *Sep. Purif. Rev.*, *44*, 109–134.

[10] N. C. Kusuma, M. Purwanto, M. A. Sudrajat, J. Jaafar, M. H. D. Othman, M. H. Abd Aziz, Y. Raharjo, M. R. Qtaishat. (2021). Fabrication and characterization of modified PVDF hollow fiber membrane coated with hydrophobic surface modifying macromolecules for desalination application. *J Environ Chem Eng.*, 9, 105582.

[11] A. Mansourizadeh, Z. Aslmahdavi, A.F. Ismail, T. Matsuura. (2014). Blend polyvinylidene fluoride/surface modifying macromolecule hollow fiber membrane contactors for CO_2 absorption. *Int J Greenh Gas Control* 26, 83–92.

[12] G. Bakeri, A.F. Ismail, D. Rana, T. Matsuura. (2012). Development of high performance surface modified polyetherimide hollow fiber membrane for gas–liquid contacting processes. *Chem Eng J*., 198-199, 327–37.

[13] M. Essalhi, M. Khayet. (2012). Surface segregation of fluorinated modifying macromolecule for hydrophobic/hydrophilic membrane preparation and application in air gap and direct contact membrane distillation. *J Member Sci*., 417–418, 163–73.

[14] R. Shoaie, J. Karimi-Sabet, S.M.A. Mousavian, P. Khadiv-Parsi, R. Moradi. (2017). Optimal modification of poly(vinylidene fluoride) membrane surface by using surface-modifying macromolecules for application in membrane distillation. *Desal Water Treat.*, 71, 62–78.

[15] V. A. Pham, J. P. Santerre, T. Matsuura, R. M. Narbaitz. (1999). Application of surfacemodifying macromolecules in polyethersulfone membranes: influence on PES surface chemistry and physical properties. *J Appl Polym Sci*., *73*, 1363–1378.

[16] A. Mansourizadeh, A. F. Ismail. (2010). CO_2 absorption with NaOH solution through the porous PVDF hollow fibre membrane contactor. *J Appl Membr Sci Technol*., *12*, 1–6.

[17] A. Mansourizadeh, A. F. Ismail, M. S. Abdullah, B. C. Ng. (2010). Preparation of polyvinylidene fluoride hollow fiber membranes for CO_2 absorption using phase-inversion promoter additives. *J Member Sci*., *355*, 200–207.

[18] E. Arjmand, A. Mansourizadeh, A. M. Ghaedi, M. Rahbari-Sisakht. (2022). Surface modification of porous polyvinylidene fluoride hollow fiber membrane by sulfonated poly(ether ether ketone) coating for membrane distillation of oily wastewater. *J Appl Polym Sci*., *139*(47), e53196.

[19] J. M. S. Henis, M. K. Tripodi. (1981). Composite hollow fiber membranes for gas separation: The resistance model approach. *J Membr Sci*., *8*(3), 233–246.

[20] T. Zarepishe, B. Honarvar, A. Mansourizadeh, N. Esfandiari. (2024). Modification of poly (vinylidene fluoride-cohexafluoropropylene) membranes by sulfonated poly (ether ether keton) coating for membrane distillation of textile wastewater. *J Text Inst*., in press.

[21] A. Mansourizadeh, A. F. Ismail. (2011). Preparation and characterization of porous PVDF hollow fiber membranes for CO_2 absorption: Effect of different non-solvent additives in the polymer dope. *Int J Greenh Gas Control*., *5*, 640–648.

[22] S. Mousavian, M. A. Ariana, A. Mansourizadeh, W. J. Lau. (2024).

Effect of stretching ratio on the structure and enactment of porous PVDF-HFP hollow fiber membranes for CO_2 absorption. *Sci Rep.*, *14,* 30285.

[23] A. C. M. Franken, J. A. M. Nolten, M. H. V. Mulder, D. Bargeman, C. A. Smolders. (1987). Wetting criteria for the applicability of membrane distillation. *J Membr Sci*., *33*, 315–28.

[24] A. Cheraghdar, M. H. Jazebizadeh, A. Mansourizadeh, M. R. Hojjati, W. J. Lau. (2025). Liquid-liquid extraction of phenolic wastewater through a surface modified poly(vinylidene fluoride-co-hexafluoropropylene) hollow fiber membrane contactor and process optimization. *J. Taiw. Inst Chem Eng., 166*, 105111.

[25] L. He, L. Li, W. Sun, W. Zhang, Z. Zhou, Z. Ren. (2016). Extraction and recovery of penicillin G from solution by cascade process of hollow fiber renewal liquid membrane. *Biochem Eng J*., *110*, 8–16.

[26] M. M. Hossain, J. Dean. (2008). Extraction of penicillin G from aqueous solutions: Analysis of reaction equilibrium and mass transfer. *Sep Purif Technol*., *62*, 437–443.