

RESEARCH ARTICLE OPEN ACCESS

PDMS Membrane Using Phenyl as Rigid Molecular Spacer for Phenol Recovery

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Received: 23 September 2024 | **Revised:** 4 March 2025 | **Accepted:** 20 May 2025

Funding: This work was funded by National Natural Science Foundation of China (22278023, 22208010), S&T Program of Hebei (24464301D) and SINOPEC Group (24-ZS-0447).

Keywords: polydimethylsiloxane | phenol | phenyl | pervaporation | thiol-ene

ABSTRACT

Polydimethylsiloxane (PDMS) is extensively utilized for the recovery of bio-alcohols, but it encounters significant obstacles in volatile organic compounds (VOCs) removal, because of the narrow size for molecules diffusion. In this work, we designed a high-efficiency diffusion channel by introducing phenyl as a spacer into PDMS chains. The monomer divinylbenzene and vinyl-terminated PDMS (vinyl-PDMS) can be chemically crosslinked with thiol-grafted PDMS (thiol-PDMS) based on thiol-ene click reaction. The result shows that the free volume radius (r_3 , r_4) has a significant increase after the introduction of divinylbenzene as a spacer, which is beneficial to the transport of phenol diffusion. After a series of optimizations involving the divinylbenzene content, pervaporation (PV) operating temperature, photoinitiator content, and viscosity of vinyl-PDMS, the prepared phenyl-PDMS showed an excellent PV performance for phenol recovery containing 10.9 of separation factor and 3959.66 g m⁻² h⁻¹ of flux as separating 0.1 wt% of phenol/water solution at 70°C. This separation performance is significantly higher than the unmodified PDMS membrane, that is, 2.05 times higher in separation factor and 3.54 times higher in flux. This study provides an effective structure design for the removal of aromatic compounds by enlarging diffusion channels and will make a great contribution to biological medicine and bioengineering.

1 | Introduction

The acceleration of urban sprawl, commercialization, and industrialization has led to the proliferation of numerous detrimental chemicals, which are deposited in wastewater. Achieving high-efficiency volatile organic compounds (VOCs) elimination or

recovery from aqueous media is critically important, presenting significant opportunities for environmental protection and economic benefit. Phenol is an important raw material in pharmaceutical and pesticide industries [1, 2]. It is also widely used in the field of biomedicine [3, 4], for example, the raw material of synthetic aspirin. However, the United States Environmental

Abbreviations: AR, analytical reagent grade; EDX, energy dispersive X-ray spectroscopy; FT-IR, Fourier transform infrared; PALS, positron annihilation lifetime spectroscopy; PDMS, polydimethylsiloxane; PEBA, poly(ether-block-amide) copolymers; PV, pervaporation; PVDF, polyvinylidene fluoride; SEM, scanning electron microscopy; VOCs, volatile organic compounds; WCA, water contact angle.

Xiangyan Li and Yan Zhuang contributed equally to this article.

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Summary

- The wastewater treatment of phenol has been attracting numerous interests in the fields of biomedical, bioengineering and biomanufacturing. The membrane separation technology has more advantages involving high efficiency and environmental friendliness for valuable organics recovery. Although the conventional PDMS membranes have been considered a high-quality separation towards phenol, their diffusion channels still show a high transport resistance due to the narrow size.
- We introduce phenyl as a spacer into PDMS chains based on the photo-induced thiol-ene click reaction. The phenyl monomer broadens the mass transfer path of PDMS to accelerate the mass transfer and increase the phenol flux, thereby reducing the investment cost of the membrane separation process.
- The recovery of high-value phenol is in line with the concept of sustainable development, and the membrane preparation process is fast, which has potential for membrane preparation process amplification.

Protection Agency designates it as the primary pollutant due to its high toxicity and carcinogenicity [5]. Its removal of phenol from wastewater becomes a key issue in the industry of biological medicine, while as a high-value chemical, its recovery meets the requirement of sustainability [6].

Current strategies for the preferential separation of VOCs, including distillation, solvent extraction, and adsorption, are characterized by high energy consumption and the need for intricate subsequent treatment processes [7]. The pervaporation (PV) membrane technology offers an energy-efficient approach to the separation of mixtures, be it organic/water or organic/organic systems, relying on a solution-diffusion process for penetrating molecules in membrane materials [8]. PV effectively bypasses the constraints imposed by thermodynamic vapor-liquid equilibrium, offering a more energy-efficient alternative to distillation. This is attributable to PV's requirement for only the latent heat of evaporation, as opposed to the substantial energy demands of the distillation process [9]. In addition, PV also owns other unique superiorities including safety and environmentally friendly without the introduction of additional chemicals [10], as well as a moderate operation temperature [11].

Among the diverse membrane materials utilized for phenol separation from aqueous solutions, for example, polyurethane [12, 13], polyimide [14], poly(ether-block-amide) (PEBA) [1, 2, 15–17], and polydimethylsiloxane (PDMS) [18–21], PDMS, serving as a benchmark for organophilic membrane materials, has garnered extensive research attention in the context of VOCs removal [22]. For instance, Ye et al. prepared an oleyl alcohol-modified PDMS membrane by blending method, result showed that the membrane had a separation factor of 6.7 and a flux rate of $230 \text{ g m}^{-2} \text{ h}^{-1}$, for the recovery of 0.5 wt% phenol from its aqueous solution at 70°C [23]. Mohammadi et al. conducted an evaluation of the performance of a PDMS membrane in the separation of binary water-phenol and ternary water-phenol-

methanol mixtures, result showed that the separation factor and the flux were 6.5 and $800 \text{ g m}^{-2} \text{ h}^{-1}$ respectively for the separation of 0.1 wt% phenol/aqueous solution at 50°C [24]. However, the transportation of aromatic compounds, such as phenol, through PDMS membranes continues to pose a significant challenge, that is, the size-limited channels, although PDMS membrane has been widely used in small-sized bio-alcohols [25–28]. The chemical modification of PDMS is the common method for improving the polymer's performance. For example, An et al. and Qin et al. introduced abundant aromatic rings and polar bonds in the polymer matrix to enhance the affinity with aromatic compounds [29, 30]. Balsara et al. prepared a polystyrene block-polydimethylsiloxane-block-polystyrene (SDS) copolymer membrane, which had permeability to VOCs [31]. However, the reports only focused on the adsorption behavior of membranes for penetrating molecules. The transport pathways within existing PDMS-based membranes mainly focus on the polymer chains' inherent free volume, unfortunately, it has not successfully provided the necessary efficiency and selectivity for the penetration of phenol.

In this work, we designed high-efficiency diffusion channels by introducing phenyl as a spacer into PDMS. Both monomer divinylbenzene and vinyl-terminated PDMS (vinyl-PDMS) can be chemically crosslinked with thiol-grafted PDMS (thiol-PDMS) based on thiol-ene click reaction, where it is also a facile membrane-formation process compared with the conventional thermal curing. Figure 1 illustrates the schematic diagram of the membrane preparation process. The monomer divinylbenzene serves as a molecular spacer, orchestrating selective pathways for the transport of aromatic molecules across the membrane. This innovative design boosts the flexibility of the methyl side groups along the polymer backbone, because of the diminished steric hindrance. Meanwhile, the resulting free volume size is expected to be increased because of the steric hindrance of phenyl. Consequently, this arrangement affords reduced resistance and additional mobility for aromatic compounds, thus enhancing their penetration through the membrane. The influence of divinylbenzene content, the viscosity of vinyl-PDMS, operational temperature, and the amount of photoinitiator on the membrane's performance were investigated. Ultimately, the longevity of the membrane's performance in PV processes was evaluated.

2 | Materials and Methods

2.1 | Materials

Phenol (AR), aniline (AR), and *n*-heptane (AR) were purchased from Aladdin, China. Photoinitiator 1173 (97%) and divinylbenzene (80%) were provided by Macklin, China. Vinyl-PDMS with *Mn* of 62597 g mol^{-1} was obtained from Shandong Dayi, China and vinyl-PDMS samples with varying molecular weight (*Mn*: 29523, 68285, 111191, and $184256 \text{ g mol}^{-1}$) were supplied by Kejunchi Technology Co., Ltd, China. Thiol-PDMS (*Mn*: 1162 g mol^{-1}) was provided by Klamar, China.

2.2 | Preparation of Membranes

The experimental procedure fabricated a ternary system comprising vinyl-PDMS, divinylbenzene, and thiol-PDMS. Tables 1

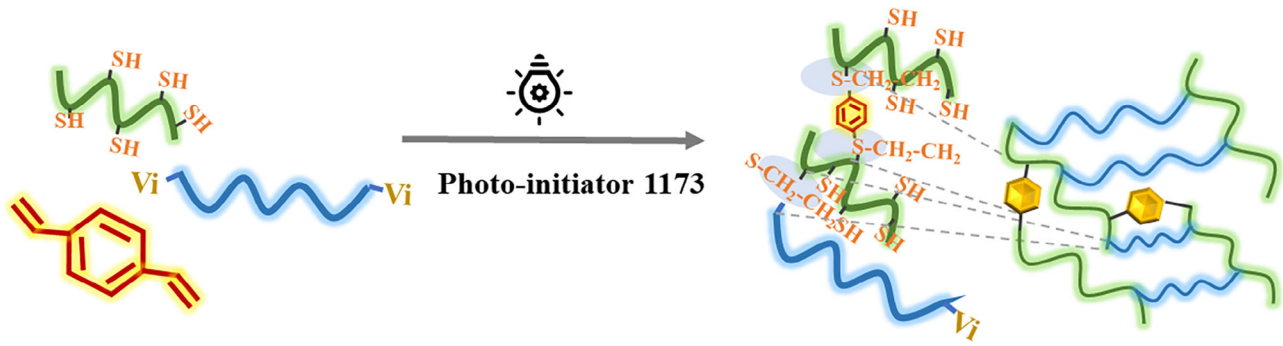


FIGURE 1 | Schematic diagram of membrane preparation.

TABLE 1 | The M_n and quality of vinyl-PDMS, thiol-PDMS, and divinylbenzene.

Membrane	Mn of vinyl-PDMS (g mol ⁻¹)	Mn of thiol-PDMS (g mol ⁻¹)	Divinylbenzene	Vinyl-PDMS(g)	Thiol-PDMS(g)
M1	29,523	1162	0.0047	0.8	0.1
M2	62,597	1162	0.0047	1.6	0.1
M3	68,285	1162	0.0047	1.8	0.1
M4	111,191	1162	0.0047	2.9	0.1
M5	184,256	1162	0.0047	4.8	0.1

TABLE 2 | The quality of vinyl-PDMS, thiol-PDMS, and divinylbenzene.

Membrane	Divinylbenzene	Vinyl-PDMS(g)	Thiol-PDMS(g)
PDMS-1	0	3.0	0.1
phenyl-PDMS-2	0.0023	2.4	0.1
phenyl-PDMS-3	0.0047	1.8	0.1
phenyl-PDMS-4	0.0071	1.2	0.1
phenyl-PDMS-5	0.0095	0.6	0.1
phenyl-PDMS-6	0.24	0	1.0

and 2 summarized the detailed reagents, and distinct membrane formulations with different M_n of vinyl-PDMS (designated as M1-6) and different proportions of vinyl-PDMS (designated as phenyl-PDMS-1-6) were prepared.

The synthesis protocol incorporated *n*-heptane as a solvent, maintaining a constant 30 wt% relative to total system mass. After achieving homogeneity through 1 h magnetic stirring, 5 wt% photoinitiator 1173 (relative to polymer mass) was introduced, followed by additional mixing for 30 min to prepare the casting solution. The degassed mixture was then coated onto PVDF substrates using an Elcometer 4340 automated applicator [32]. And the substrate PVDF preparation followed our previous methodology [33]. A critical curing procedure was implemented by positioning the liquid coating 10 cm beneath a 365 nm UV light, achieving complete membrane formation through irradiation in 10 min.

2.3 | Characterization

The wettability characteristics of the membranes were evaluated through water contact angle (WCA) using a JC2000D3 optical contact angle measuring instrument. The microstructures of the membrane cross-sections were observed using scanning electron microscopy (SEM, Hitachi-SU8020) equipped with energy-dispersive x-ray spectroscopy (EDX) for elemental mapping of silicon distribution. Fourier transform infrared (FT-IR) spectroscopy was performed with a Nicolet 8700 spectrometer. The molecular weights of vinyl-PDMS and thiol-PDMS were determined by gel permeation chromatography (GPC, Waters 1515) using tetrahydrofuran as the mobile phase. Free volume characteristics within the membranes were investigated using the PALS. The parameters including the free volume cavity radius r_i , the ortho-positronium (o-Ps), pick-off lifetime τ_i , the electron layer thickness Δr (0.1656 nm), and the free volume (FFV) were determined [34].

$$\tau_i = \frac{1}{2} \left[1 - \frac{r_i}{r_i + \Delta r} + \left(\frac{1}{2\pi} \right) \sin \left(\frac{2\pi r_i}{r_i + \Delta r} \right) \right]^{-1} \quad (1)$$

$$\text{FFV} = \frac{4\pi}{3} (r_3^3 I_3 + r_4^3 I_4) \quad (2)$$

2.4 | PV Performance

PV performance was evaluated on the custom-fabricated apparatus following the method in our previous studies [10, 32]. During the process of phenol recovery, the PV device system maintained vacuum conditions (<100 Pa) through a vacuum pump (model 2XZ-2, manufactured by Shanghai Jingqi Instrument). 0.1 wt% phenol/water solution was loaded into the liquid reservoir and circulated using a peristaltic pump (L100-1S-2). The membrane's

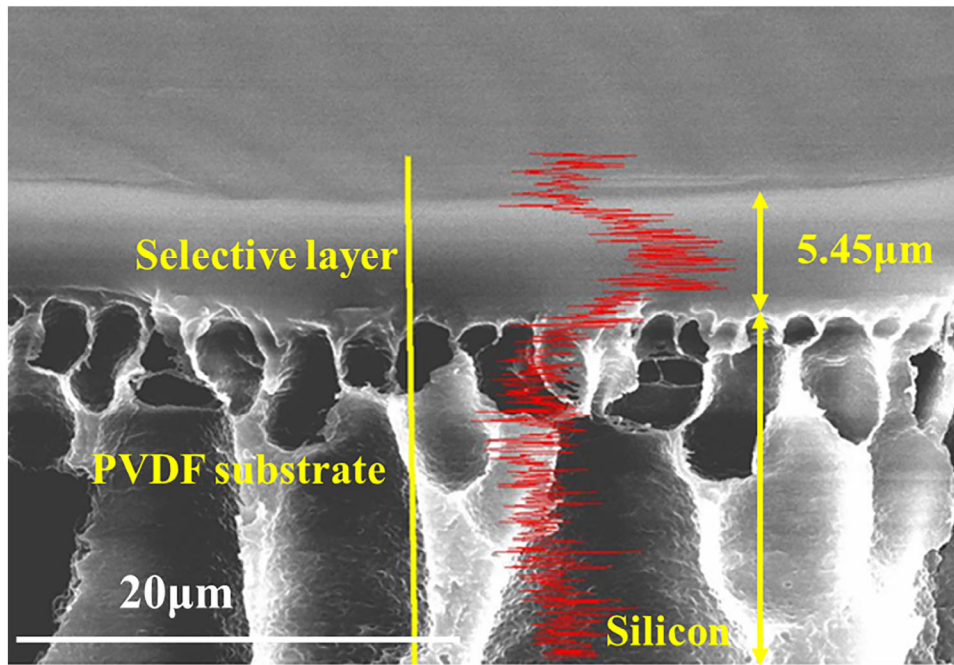


FIGURE 2 | Cross-sectional SEM images and Si EDX mapping of phenyl-PDMS-3 membrane.

effective area was 28.26 cm². The phenol concentration in both the feed (x_e) and permeate (y_e) was quantitatively determined using a Shimadzu GC-14C gas chromatograph. The total flux (J , g m⁻² h⁻¹), separation factor (β), and PV separation index (PSI) were subsequently calculated according to the subsequent equations [35]:

$$J = \frac{W}{A \times t} \quad (3)$$

$$\beta = \frac{y_e / (1 - y_e)}{x_e / (1 - x_e)} \quad (4)$$

$$\text{PSI} = J \times (\beta - 1) \quad (5)$$

where W denotes the weight of the permeate (g), A signifies the membrane's contact area (m²), t represents the duration of the phenol recovery process (h)

3 | Results and Discussion

3.1 | Characterizations of Membranes

The microstructure of the cross-section of phenyl-PDMS-3 membrane is observed by SEM. As shown in Figure 2, taking phenyl-PDMS-3 as an example, the thickness of the membrane is measured to be 5.45 μm. The combination of the selective layer and the PVDF substrate is dense and defect-free. The finger-like pores adjacent to the PVDF surface and the honeycomb-like pores are conducive to diminishing the mass transfer resistance encountered by molecules [10, 36]. Elemental mapping of silicon via EDX further substantiates the interfacial correlation between the selective layer and substrate [37]. It can be seen from the EDX-SEM image that the separation layer of the membrane in the cross-section image is well contacted to the PVDF substrate,

without the penetration of the membrane liquid and no obvious defects.

In order to verify that phenyl groups were introduced into PDMS by thiol-ene click reaction, the surface chemical properties of thiol-PDMS, vinyl-PDMS, and phenyl-PDMS-3 membrane were comparatively analyzed using FT-IR spectroscopy. As shown in Figure 3, the characteristic peaks observed at 1412 and 1257 cm⁻¹ correspond to the asymmetric and symmetric deformation vibrations of the Si-C bond, respectively [38]. The peaks at 863 and 785 cm⁻¹ are attributed to the stretching vibrations of Si-O and Si-C bonds, respectively [39]. The peaks at 1086 and 1008 cm⁻¹ are assigned to the asymmetric stretching vibrations of the Si-O-Si bridging bonds [40]. Concurrently, in contrast to thiol-PDMS, phenyl-PDMS-3 does not exhibit a thiol stretching vibration peak at 2830 cm⁻¹, which indicates that the thiol-ene click reaction occurred [39, 41–43]. According to the solution-diffusion model, the surface hydrophobicity of the membrane is the key to achieving highly selective separation of organic matter [44]. Figure 4 shows the phenyl-functionalized membranes exhibit high WCAs, varying between 107.4° and 121.2°. This can be explained because the phenyl group in divinylbenzene is hydrophobic [45], so the increase of divinylbenzene within the selective layer increases the hydrophobicity of the membrane surface [46], thereby enhancing the affinity of the membrane to phenol [20]. Furthermore, with the increase of phenyl content, the bulk physical interactions among polymer chains, such as π - π interactions, are enhanced [47], and the increase of crosslinking density will increase the interaction between PDMS and aromatic molecules, thus improving the hydrophobicity of phenyl-PDMS membranes [10, 48].

In the separation layer, the preferential diffusion channel of the penetration molecules directly determines the PV performance [49]. Table 3 shows that the free volume radius (r_3) increases

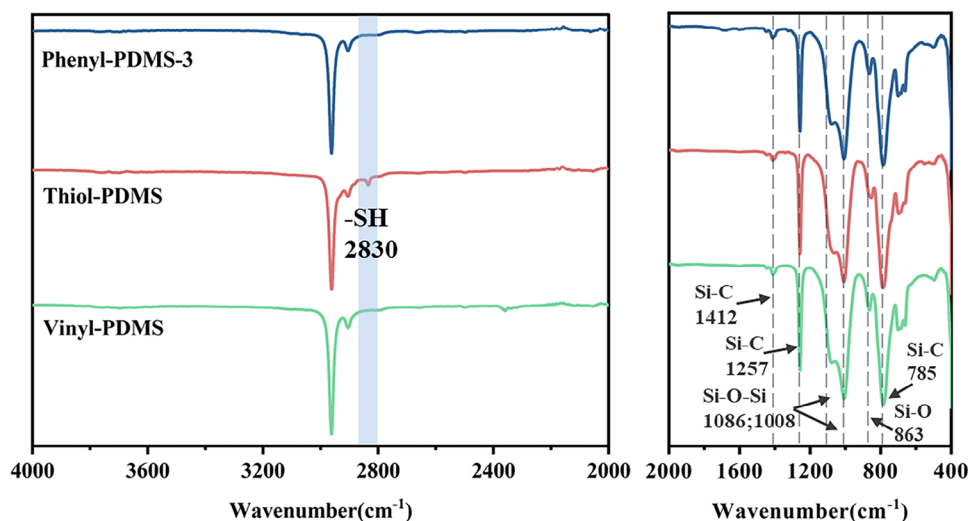


FIGURE 3 | FT-IR spectra of the vinyl-PDMS, thiol-PDMS, and phenyl-PDMS-3.

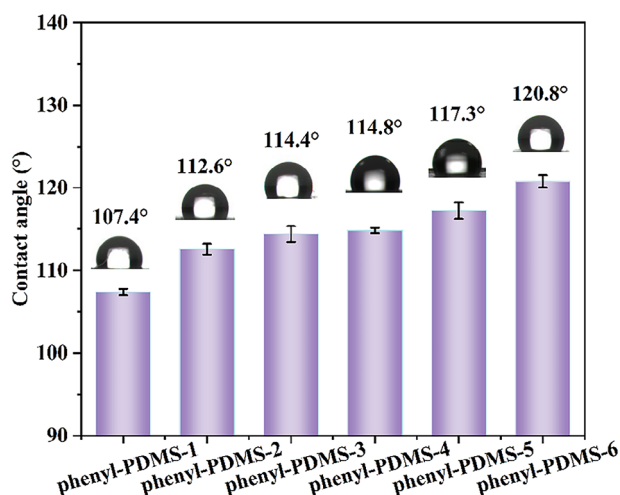


FIGURE 4 | Water contact angle of phenyl-membranes.

TABLE 3 | Free volume radius (r_3 , r_4) of PDMS-1, phenyl-PDMS-1, and phenyl-PDMS-6.

Membrane	r_3 (nm)	r_4 (nm)
PDMS-1	0.0852	0.3929
phenyl-PDMS-2	0.1002	0.3939
phenyl-PDMS-3	0.1236	0.3988

from 0.0852 to 0.1236 nm after the introduction of divinylbenzene as a spacer, which is beneficial to the transport of phenol diffusion. The monomer divinylbenzene is expected to become a molecular spacer to create selective transport highways for aromatic molecules through the membrane, which can expand the chain distance and make the methyl side groups on the main skeleton have higher mobility due to lower steric hindrance. Additionally, the phenyl spacer makes the polymer segments loosely stacked, thereby inhibiting the coordinated movement of the main chain. Accordingly, it provides lower resistance and additional degrees of freedom for aromatic compounds, thereby

promoting its penetration. The equivalent pore sizes (r_4) of the three PDMS samples are in the range of 0.3929–0.3988 nm, and the size of the free volume available for phenol or water transport changes slightly. The possible reason is that the change of cavity caused by the change of chain conformation is almost offset by the variation of space occupied by the substituted side groups.

3.2 | PV Performance

3.2.1 | Divinylbenzene Contents

This work presents a rapid preparation strategy for phenyl-PDMS PV membranes via thiol-ene click reaction, with the investigation of divinylbenzene contents on membrane PV performance. The approach utilizes divinylbenzene as a spacer to increase mass transfer channels within the PDMS matrix. The results demonstrate that the mixture of divinylbenzene and thiol-PDMS achieves effective cross-linking through UV-induced photopolymerization to form separation membranes. The incorporation of phenyl groups enhances phenol affinity through π - π interactions, thereby improving preferential adsorption during permeation [20]. As depicted in Figure 5A, the separation factor increases remarkably from 10.3 (PDMS-1) to 21.2 (phenyl-PDMS-6) when separating a 0.1 wt% phenol solution at 60°C. By adjusting the molar ratio of vinyl-PDMS to divinylbenzene while maintaining a constant 1:1 thiol-to-vinyl stoichiometry, the total flux shows a non-monotonic trend. The total flux initially increases from 807.86 g m⁻² h⁻¹ to a maximum of 2859.34 g m⁻² h⁻¹ and then declines to 994.69 g m⁻² h⁻¹ with increasing divinylbenzene content. This phenomenon can be attributed to the fact that the divinylbenzene spacer reduces mass transfer resistance by expanding free volume; however, excessive divinylbenzene induces tight crosslinking owing to its small molecular size, ultimately limiting molecular transport [50]. Figure 5B reveals that the phenyl-PDMS-3 membrane achieves optimal phenol/water permeation performance. Notably, the separation factor gradually decreases from 10.32 to 9.77 before rising to 21.16. This could be attributed to the enhanced hydrophobicity by introducing phenyl groups confirmed by contact angle measurements in Figure 5,

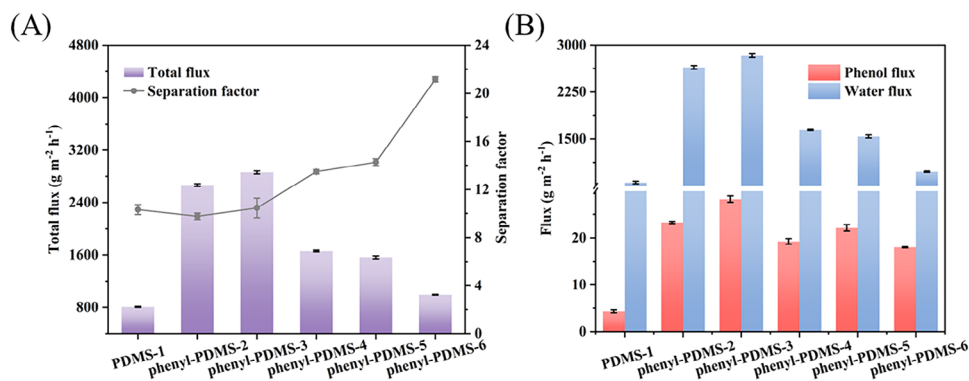


FIGURE 5 | Effect of divinylbenzene content on PV performance: (A) total flux and separation factor; (B) phenol flux and water flux of the phenyl-PDMS-3 for separating phenol.

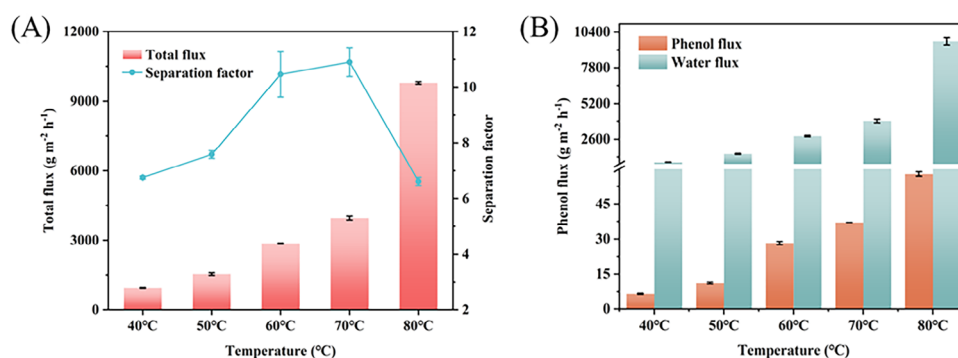


FIGURE 6 | Effect of feed temperature (feed concentration: 0.1 wt%) on the membrane (A) total fluxes and separation factors; (B) phenol flux and water flux of the phenyl-PDMS-3 for separating phenol.

thus improving phenol selectivity through preferential sorption. The hydrophobic barrier formed by phenyl moieties effectively impedes water permeation and facilitates phenol transport to improve phenol affinity. The separation factor of the phenyl-PDMS-2 membrane reduces because of the enhancement initial flux induced by the trade-off effect. The phenyl-PDMS-3 membrane similarly exhibits excellent separation performance for 0.1 wt% aniline and 5 wt% ethanol aqueous solutions at 60°C (Figure S1), confirming its versatility in organic compound recovery.

3.2.2 | Feed Temperature

The influence of feed temperature on the separation performance of phenyl-PDMS-3 membrane is evaluated using a 0.1 wt% phenol/water solution at a temperature range of 40°C–80°C. As shown in Figure 6A, the total flux exhibited an obvious increase from 937.9 to 9784.0 g m⁻² h⁻¹ with increasing temperature. This enhancement was attributed to two synergistic effects: (1) Increased polymer chain mobility at increased temperatures enhances free volume fraction (FFV), thereby reducing mass transfer resistance and accelerating the diffusion rates of both phenol and water molecules [51, 52]; (2) Increasing temperature strengthen transmembrane differential pressure, providing additional driving force for permeation [1, 51, 53]. Correspondingly, Figure 6B demonstrates a simultaneous increase in both phenol and water fluxes with enhanced temperature.

The separation factor increased from 6.8 to 10.9 between 40°C and 70°C before decreasing to 6.6 at 80°C (Figure 6A). The initial

improvement is consistent with solution-diffusion theory and membrane hydrophobicity. Membrane swelling promotes phenol accumulation at the membrane surface while creating expanded transport channels for aromatic compounds with the increased temperature [18, 54, 55]. However, the water molecule exhibits faster diffusion than phenol [15, 56] owing to the smaller size of water molecules beyond 70°C. It can explain the subsequent decline in separation factor, which is consistently reported in PDMS-based PV studies [53, 55–57].

3.2.3 | Photoinitiator Contents

The photoinitiator plays a pivotal role within the photocuring system, directly affecting both the efficiency of polymerization and membrane properties. The influence of photoinitiator concentration (5–13 wt%) on the separation efficacy of phenyl-PDMS-3 membrane is assessed under 70°C and 0.1 wt% phenol/water feed concentration. As shown in Figure 7A, total flux demonstrates an inverse correlation with photoinitiator content, decreasing from 3959.7 g m⁻² h⁻¹ at 5 wt% to 1273.3 g m⁻² h⁻¹ at 13 wt%. A similar decreasing trend is observed in phenol/water flux (Figure 7B), which can be attributed to the elevated crosslinking density induced by higher photoinitiator concentration. The resulting compact network structure enhances transport resistance for phenol molecules [44]. The separation factor initially increases from 10.9 at 5 wt% to a maximum of 18.7 at 11 wt%, followed by a decline to 14.7 at 13 wt% (Figure 7A). The increased separator can be explained as the initial enhancement is attributed to

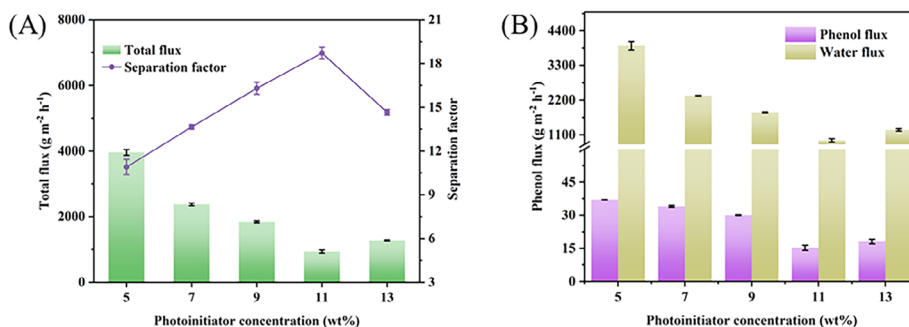


FIGURE 7 | Effect of photoinitiator concentration (feed temperature: 70°C, feed concentration: 0.1 wt%) on the membrane (A) total fluxes and separation factors; (B) phenol flux and water flux of the phenyl-PDMS-3 for separating phenol.

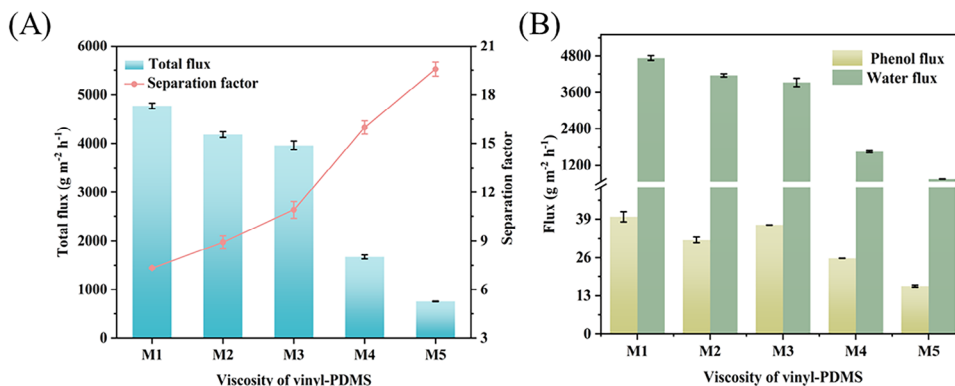


FIGURE 8 | Effect of viscosity of casting solution (feed temperature: 70°C, feed concentration: 0.1 wt%) on the membrane (A) total fluxes and separation factors; (B) phenol flux and water flux of the phenyl-PDMS-3 for separating phenol.

improved membrane hydrophobicity that promotes preferential phenol adsorption [58], and the size exclusion effects restrict water transport within narrowed channels [28, 58]. Consequently, the transference capability of water has decreased remarkably [59]. However, excessive photoinitiator content (13 wt%) leads to a decreased separation factor, which is ascribed to the light shielding effect that impedes complete curing [25, 60]. Other works have also reported similar phenomena [28, 44]. According to the study of Si et al., similar results were noted in the separation of furfural through the polymerization of PDMS membrane initiated by photoinitiator TPO-L [44].

3.2.4 | Vinyl-PDMS Viscosity

The influence of vinyl-PDMS viscosity on phenol separation performance at 70°C was also investigated. Liu et al. observed that casting solution viscosities below 45 cp cause the PDMS solution to penetrate into the pores of the PVDF substrate, this leads to the formation of non-selective defects in the selective layer [61]. Nevertheless, high molecular weight polymer exhibits serious chain entanglement, which impedes the mobility of active sites, thereby compromising polymerization efficiency [62]. The viscosity of the reactants plays a critical role in creating a close-knit, defect-free selective layer on PVDF substrate [55]. Consequently, it is crucial to determine the optimal PDMS viscosity to enhance the separation efficacy of polymeric membranes. This work applied vinyl-PDMS with different molecular weights characterized by GPC to evaluate the effect of viscosity on separation performance.

The total flux of phenol/water solution decreases from 4769.9 to 758.5 g m⁻² h⁻¹ (Figure 8A), and phenol/water flux also shows a downward trend (Figure 8B) with increasing viscosity while separation factors improved from 7.3 to 19.6 (Figure 8A). Elevated viscosity enhances polymer chain interconnection while restricting chain mobility [63], promoting the formation of highly cross-linked networks [64]. In addition, higher viscosity solutions could form stronger interactions between polymer and substrate, resulting in thicker selective layers that generate higher transport resistance [62]. Conversely, casting solution with low viscosity tends to penetrate the substrate, forming non-selective layers [61].

3.2.5 | Stability and Comparison

To evaluate the stability of phenyl-PDMS membranes for wastewater treatment, the separation process was conducted through high-temperature operations and long-term testing. The phenyl-PDMS-3 membrane showed exceptional operational stability during 120 h in 0.1 wt% phenol/water solution at 70°C. As illustrated in Figure 9A, the membrane maintained consistent separation performance through the period, demonstrating stable phenol separation efficiency without significant change. As shown in Figure 9B and Table S1, the phenol-PDMS membranes presented in this work exhibit significant competitive advantages in comparison to other polymeric membranes, especially the PDMS membranes. It is evident that the total flux of most polymer membranes is generally insufficient to be considered

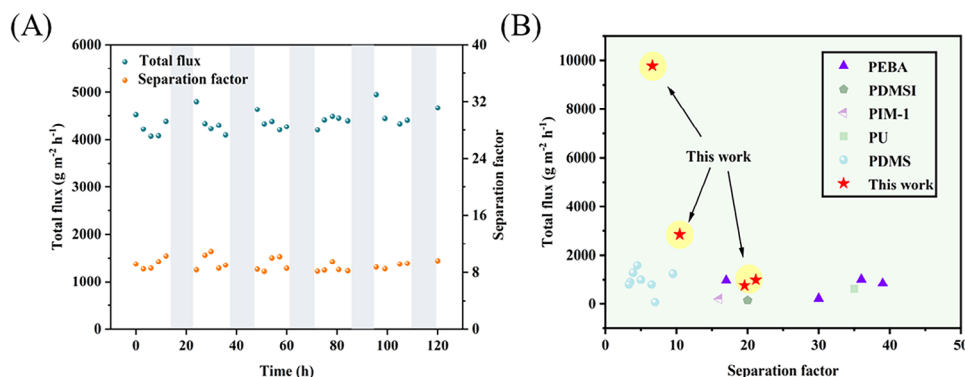


FIGURE 9 | (A) Long-term separation performance of phenyl-PDMS-3 membrane; (B) Comparison with the polymer membrane reported before (more details in Table S1).

competitive ($<500 \text{ g m}^{-2} \text{h}^{-1}$). While most polymer membranes exhibit limited competitiveness due to the inferior total flux ($<500 \text{ g m}^{-2} \text{h}^{-1}$), and some high-flux membranes suffer from inadequate separation factors, the phenyl-PDMS design addresses these limitations. Although PEBA membranes demonstrate comparable separation factors, their practical application is restricted by structural limitations as free-standing configurations, which impacts long-term operational stability [65]. The incorporation of phenyl groups as rigid molecular spacers optimizes mass transfer channels, achieving the high flux ($2859 \text{ g m}^{-2} \text{h}^{-1}$) and favorable separation factors (10.5), and it has application potential in the recovery of phenolic wastewater produced in the field of biomedicine.

4 | Concluding Remarks

This study presents a facile approach for enhancing the preferential transport of phenol over water through organophilic PDMS membranes by incorporating phenyl groups as rigid molecular spacers. Herein, PV membranes were prepared through thiol-ene click reaction using divinylbenzene as a structural spacer. The phenyl-PDMS-3 membrane emerges as an exceptional candidate for the separation of 0.1 wt % phenol in aqueous solutions, demonstrating a separation factor of 10.5 and a total flux of $2859 \text{ g m}^{-2} \text{h}^{-1}$. The critical influences of operation temperature, photoinitiator concentration, and vinyl-PDMS viscosity on membrane performance were investigated. Notably, the fabricated PV membranes demonstrated superior stability, maintaining consistent separation efficiency during continuous extraction of phenol aqueous solutions for over 120 h. The incorporation of phenyl spacers in the membrane provides a novel strategy for improving separation performance. This research offers an environmental and energy-efficient strategy for phenol recovery, especially for biomedical wastewater treatment.

Acknowledgments

This work was funded by National Natural Science Foundation of China (22278023, 22208010), S&T Program of Hebei (24464301D) and SINOPEC Group (24-ZS-0447).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting information