Fluorinated PDMS membrane with anti-biofouling property for *in-situ* biobutanol recovery from fermentation-pervaporation coupled process

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** A R T I C L E   I N F O**

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- Anti-biofouling
- PDMS membrane
- Butanol
- Pervaporation
- Fermentation coupled process

**A B S T R A C T**

Hydrophobic pervaporation membranes such as polydimethylsiloxane (PDMS) have shown great potential for biofuels recovery from fermentation process, which however face the challenge of biofouling issue. In this work, a new kind of anti-biofouling PDMS membrane was developed by creating an ultra-low energy surface via a facile crosslinking reaction between fluorosilane and PDMS. The chemical properties and wettability of the membrane surface were characterized by IR, XPS and contact angle measurements, in which the effect of chemical groups on the surface free energy was studied. The performance of PDMS membranes were evaluated in a typical acetone-butanol-ethanol (ABE) fermentation-pervaporation coupled process. The results demonstrated that the introduction of fluoroalkyl groups highly reduced the surface energy of PDMS membrane, thereby achieving excellent hydrophobicity and lipophobicity at the same time, and successfully alleviating microbial adhesion onto the membrane. As a result, the fluorinated PDMS membrane exhibited excellent anti-biofouling property, as well as much higher stabilized total flux (0.74 vs 0.36 kg/m\(^2\)h) and ABE separation factor (21.8 vs 7.1) than the pristine PDMS membrane as coupling fed-batch fermentation for 140 h. In addition, a significant enhancement in ABE productivity (e.g., 51% higher than batch fermentation) was obtained in the fluorinated PDMS membrane coupled fed-batch fermentation process.

1. **Introduction**

Biobutanol is recognized as an important solvent and renewable fuel additive that can be manufactured by microbial fermentation of the low-cost feedstocks [1]. With the consumption of energy resources and the advancement of separation technology, ABE (i.e., acetone, butanol and ethanol) fermentation became the second biotechnological and produce process [2,3]. To overcome the inhibition of solvents on cell growth, fermentation integrated with pervaporation separation process has attracted general interests [4]. Many kinds of membranes have been studied for separation of butanol/water mixtures, ABE/water mixtures and ABE fermentation broth [5,6]. A few of them such as polydimethylsiloxane (PDMS) [7–11], poly[1-(trimethylsilyl)-1-propyne (PTMSP) [12] have been coupled with ABE fermentation for *in-situ* butanol recovery. Among these membranes, PDMS membrane is the most widely studied owing to its high performance for butanol/water separation and easy fabrication.

Fouling commonly occurs in membrane separation process, leading to deterioration of membrane properties either temporarily or permanently, and thus shortening membrane life eventually [13–16]. During the fermentation-pervaporation integration process, once the bacteria are deposited, they grow, multiply, and contribute to biofilm formation on membrane surface [17–20]. The biofouling is a great challenge for membrane towards long-term operation process [21]. Yeon et al. considered that the biofouling layer on the membrane surface consists of both deposited microbial flocs (e.g., mixed liquor suspended solid) and growing microorganisms on the membrane surface (e.g., biofilm) [22]. In our previous work, during the ABE fermentation-pervaporation coupled process, the growth of microbes on the PDMS membrane surface dramatically declined the biobutanol recovery performance [23]. Fadeev et al. focused on the application of ABE fermentation with PTMSP-based pervaporation integrated process [24]. They attributed the decrease of membrane performance to the lipid absorption in the free volumes of polymeric membrane.

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It’s very important and highly desirable to develop hydrophobic pervaporation membrane with anti-biofouling property that could be much more favorable for treating fermentation broth especially for the application in fermentation-pervaporation coupled process. However, it is particularly challenging for a hydrophobic membrane to achieve anti-biofouling property, because the bio-foulants mainly consisting of proteins are often hydrophobic which would preferentially adsorb onto the hydrophobic membrane surface and form a strong adhesion with membrane [25,26]. Conventionally, lowering the surface hydrophobicity is effective to improve the biofouling-resistance of membrane. However, this approach is not suitable for hydrophobic pervaporation membrane since its separation performance will be also decreased with the hydrophobicity. Thus, it’s critical to overcome the assumed trade-off between separation performance and anti-biofouling property for the hydrophobic membranes that are widely used for biofuels recovery from fermentation broth.

It’s also interesting to notice that surfaces with both hydrophobicity and lipophobicity, namely amphiphobic surfaces have received increasing attention in recent years [27]. Compared with hydrophobic surface, creating lipophobic surface that resist wetting of organic liquids is more challenging since the much lower surface tension of organic liquids than water [28]. Generally, fluoro-derived compounds were introduced to enhance the surface hydrophobicity and lipophobicity. The amphiphobic membranes were also studied for membrane separation [29] mainly focused on water desalination [30] and oil/water separation [31]. However, it remains a challenge to develop pervaporation membrane with both hydrophobicity and lipophobicity, probably due to the limitation in membrane materials and fabrication approaches.

In this work, we proposed a new kind of anti-fouling hydrophobic membrane by introducing fluoroalkyl groups to create an ultra-low energy surface via a facile crosslinking reaction between fluorosilane and hydroxyl-terminated PDMS. Specifically, a traditional crosslinker for PDMS membrane, tetraethyl orthosilicate (TEOS) was replaced with 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFDTES). As a result, hy.

2. Experimental

2.1. Materials

PDMS (a,ω-dihydroxypolydimethylsiloxane, average molecular weight: 6000) was supplied by Shanghai Resin Factory, China. Tetraethyl orthosilicate (TEOS, 98%), dibutyltin dilaurate (DBTOL, 95%), n-butanol (AR) and n-heptanol (AR) were supplied by Shanghai Lingfeng Chemical Reagent Co., Ltd, China. 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFDTES) was purchased from Saen Chemical Technology Co., Ltd, China. Tubular ceramic substrates were homemade with average pore size of 200 nm and o.d./i.d. of 12/8 mm.

2.2. Membrane preparation

After dissolving PDMS in n-heptanol, TEOS or PFDTES and DBTOL were added with weight ratio for PDMS/n-heptanol/TEOS or PFDTES/DBTOL of 1/10/0.5-0.9/0.5. The PDMS/ceramic composite membrane was fabricated by following our previous study [32]. The resulting mixtures were stirred at 20 °C until its viscosity was suitable for dip-coating. The mixtures were dip-coated on the outer surface of the ceramic substrate for 1 min. In order to prevent PDMS casting solution

Fig. 1. Schematic of preparation of (a) pristine PDMS membrane and (b) fluorinated PDMS membrane via the condensation reaction between silane crosslinker and hydroxyl-terminated PDMS.
from immersing on the inner surface of the tubular ceramic support, one end of ceramic tube was blocked by a rubber plug during the coating process. After drying at 20 °C overnight and subsequently heating at 120 °C for 12 h, the PDMS composite membranes were fabricated. The membrane prepared by using TEOS crosslinked PDMS is named as pristine PDMS membrane, and the membrane prepared by using PFDTES crosslinked PDMS is named as fluorinated PDMS membrane.

2.3. Membrane characterizations

The membrane morphology was examined by field emission scanning electron microscopy (FESEM, Hitachi-4800, Japan). The membrane after using in fermentation broth was treated with a “fixing step” described in our previous work [23]. Infrared spectra were recorded in an ATR-FT-IR spectrophotometer (AVATAR-FT-IR-360, Thermo Nicolet, USA) with range of 4000-400 cm⁻¹ 32 scans and resolution of 4 cm⁻¹ for each spectrum. The chemical composition of the membrane surface was investigated by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250, USA). The static contact angles of the membrane were measured by Sessile liquid drop method using contact angle measurement system (DSA100, Krüss, Germany). Each data was based on the average of contact angles at three different sites with the error of ~1°.

Owens-Wendt geometric mean method was employed to calculate the surface free energy of the PDMS membrane using its surface contact angles with two kinds of liquids [33]. Harmonic mean equation was used to sum the dispersive and polar contributions of the surface free energy. Contact angles against at least two liquids with different surface tensions and known values of θᵣ and θₛ are measured:

\[ (1 + \cos \theta) \cos \theta = \left( \sqrt{\gamma_{\text{l}}}, \gamma_{\text{s}} \right) \]  
\[ \gamma_s = \gamma_{\text{l}} + \gamma_{\text{d}} \]  

where \( \gamma \) refers to surface tension (surface free energy), the subscripts \( l \) and \( s \) refer to liquid and solid, and the superscripts \( d \) and \( p \) refer to dispersive and polar components.

2.4. Pervaporation measurement and ABE fermentation-pervaporation coupled process

The membrane with an effective membrane area of 48.98 cm² was installed in a tubular membrane module described previously [23]. The temperature of feed tank or fermenter was controlled at 37 °C, and the feed flow rate was kept at 15 L/h. The pressure of permeate side was below 300 Pa. The compositions of feed and permeate were analyzed by a gas chromatography (GC-2014, Shimadzu, Japan). The separation performance is evaluated by total flux (\( J \)) and separation factor (\( \beta \)):

\[ J = \frac{M}{At} \]  
\[ \beta = \frac{y_A / y_B}{x_A / x_B} \]

where \( M \) is weight of the permeate (g), \( A \) is the effective membrane area (m²), and \( t \) is the permeation time (h); \( y \) and \( x \) are the weight fractions of components \( A \) (acetone, butanol or ethanol) or \( B \) (water) in the permeation and feed, respectively.

A fed-batch ABE fermentation with 1.5L working volume was carried out by following our previous study [34]. As the butanol concentration in the broth reached 6.0 g/L, the sterilized membrane module was integrated with the fermenter to conduct in-situ ABE removal [35]. A UV–visible spectrophotometer (Lambda-25, Perkin-Elmer, USA) was used to measure the optical density with wavelength of 600 nm. Residual glucose concentration was analyzed by a 1200 series HPLC system (Agilent Technologies Inc.).

3. Results and discussion

3.1. Preparation of fluorinated PDMS membranes

The effect of crosslinker concentration on the membrane separation performance was studied to optimize the fabrication of fluorinated PDMS membrane. The mass ratio of PDMS/fluorosilane was varied from 100/10, 100/15, 100/20, 100/25, 100/30 to 100/40. As shown in Fig. 2, with increasing the crosslinker concentration, the total flux was decreased while the separation factor was increased firstly and then remained unchanged. The crosslinking density of the PDMS would be increased by using higher crosslinker concentration, which would decrease the free volumes of PDMS membrane and thus reduce the total flux. The reduced separation factor at lower crosslinking density indicated the present of some minor non-selective defects in the PDMS membrane, which can be eliminated by increasing the crosslinker concentration to 20%. The optimized fluorinated PDMS membrane (PDMS/fluorosilane: 100/20) exhibited outstanding separation performance for n-butyol/water separation, with total flux of 0.81 kg/m²·h and separation factor of 27.6. As a control, using the traditional crosslinker (TEOS) with same concentration (20 wt%), the pristine PDMS membrane showed 0.89 kg/m²·h for total flux and 23.5 for separation factor. The slight difference in total flux between pristine and fluorinated PDMS membranes was due to the variation in membrane thickness (see SEM result in Fig. 3). The higher separation factor achieved in the fluorinated PDMS membrane can be attributed to the fluoroalkyl-enhanced hydrophobicity which will be discussed in the results of contact angle measurement.

3.2. Morphologies and surface properties of PDMS membranes

SEM was used to characterize the morphologies of PDMS membrane coated on the outer surface of tubular ceramic support. As shown in Fig. 3, a dense and uniform PDMS membrane layer was closely attached on top of the porous ceramic support. The surface of either pristine or fluorinated PDMS membrane was very smooth without any visible defects. During coating the outer surface of ceramic support, the PDMS solution penetrates into the ceramic support to form a clear transition layer. By further optimizing the coating conditions, a suitable separation layer could be obtained on the ceramic support with 10 wt% PDMS solution and dipping for 60s. An average membrane thickness of pristine PDMS and fluorinated PDMS were 6.4 µm and 7.5 µm, respectively. The slightly thicker membrane for the fluorinated PDMS lead to the lower total flux observed in Section 3.1.

The chemical groups on the membrane surface were critical to
determine the interactions of separation components and foulants with membrane surface, which were analyzed by FT-IR and XPS for PDMS membranes in this work. As shown in Fig. 4, the peaks located at 1445, 1412 and 1256 cm\(^{-1}\) belonged to the deformation vibration of methyl groups (\(\delta(CH_3)\)) [36]. Meanwhile, the characteristic bands owing to asymmetric stretching (\(\nu_{as}(CH_3)\)) and rocking (\(\rho(CH_3)\)) of the CH\(_3\) groups are focused on 2962 and 783 cm\(^{-1}\). In addition, PDMS has double peaks about 1076 and 1005 cm\(^{-1}\) due to the asymmetric stretching vibration of Si–O–Si group (\(\nu(Si–O)\)). Two peaks at 1207 and 1150 cm\(^{-1}\) corresponding to the characteristic absorption peak of C–F bond [37] were observed in fluorinated PDMS membranes, confirming the successful introduction of fluoroalkyl groups into the membrane surface.

The XPS results of pristine and fluorinated PDMS membrane are depicted in Fig. 5. The main elements including Si, O and C, which are resulted from the main chains (Si–O–Si) and side groups (–CH\(_3\)) of PDMS, were found in both pristine and fluorinated PDMS membranes. Clearly, F1s signal at a binding energy around 689.0 eV appeared in the fluorinated PDMS membrane, confirming the presence of fluorinated groups (–CF\(_2\), –CF\(_3\)) on the membrane surface [38]. Fig. 5b exhibited the C1s spectra of the two kinds of PDMS membranes, a single peak at 284.7 eV was observed, which is consistent with element C in a methyl side groups attached to the Si–O–Si main chains of PDMS. With introducing the fluoroalkyl groups (–(CH\(_2\))\_2–(CF\(_2\))\_2–CF\(_3\)) via PFDTES crosslinking, the C1s line in the fluorinated PDMS membrane showed peak shift for –C-C– from 286.2 eV to 285.9 eV, as well as new peaks associated with fluorinated groups as follows: (i) –CF\(_3\) at 294.6 eV, (ii) –CF\(_2\)- at 292.3 eV, (iii) –C–CF\(_2\)- at 287.0 eV [39]. FT-IR and XPS results suggested that fluoroalkyl groups was successfully incorporated into the PDMS network and present on the membrane surface, providing the chemical basis for tuning the molecular interactions of membrane surface with microbes and products in the fermentation broth.

Measurements of liquid-solid contact angles are commonly used to evaluate surface free energy and wettability of a material. As a liquid deposited on a solid substrate, the wetting tendency is larger, the smaller the contact angle or the surface free energy is [40,41]. In this work, water was used as a kind of polar liquid and diiodomethane was selected as a kind of nonpolar liquid for the contact angle test. As shown Fig. 6, both pristine and fluorinated PDMS membranes exhibit water contact

Fig. 3. SEM images of (a-b) pristine PDMS membrane and (c-d) fluorinated PDMS coated on the ceramic support. (a) and (c) cross-section, (b) and (d) surface.

Fig. 4. FT-IR spectra of pristine and fluorinated PDMS membranes. (a) full wavenumber range; (b) selected wavenumber range to highlight the difference between the two membranes.
angles much higher than 90°, suggesting a hydrophobic nature as expected for PDMS pervaporation membranes [42]. The hydrophobicity of PDMS membranes can be attributed to the methyl groups on the surface, which was further enhanced by introducing the fluoroalkyl groups [-CH$_2$]$_n$-(CF$_2$)$_m$-CF$_3$], as evidenced by the water contact angle increasing from 113.5° to 125.5°. Moreover, the diiodomethane contact angle of 102° on the fluorinated PDMS membrane suggested both hydrophobic and lipophobic surface property, which could not be achieved for the pristine PDMS membrane (diiodomethane contact angle of 77.5°).

To further understand the distinct wettability observed in pristine and fluorinated PDMS membranes, the surface free energy was calculated using the Owens-Wendt’s two-liquid geometric mean method [33]. The calculation results are summarized in Table 1. As expected of nonpolar, non-hydrogen-bonding surfaces such as PDMS membrane, the dispersion contribution was largely dominant, with the polar contribution being minimal. Compared with the pristine PDMS membrane, the fluorinated PDMS membrane possessed a much lower surface energy because of the both substantial hydrophobicity and lipophobicity resulting from the introduced surface fluoroalkyl groups [43].

Overall, the introduction of fluoroalkyl groups into the membrane by using fluorosilane to crosslink PDMS successfully created a desirable surface that is hydrophobic and lipophobic at the same time. The

![Fig. 5. XPS spectra of pristine and fluorinated PDMS membranes. (a) full scan; (b) C1s scan.](image1)

![Fig. 6. Static contact angle on the surface of PDMS membranes: Image of contact angle for (a) water on pristine PDMS. (b) water on fluorinated PDMS. (c) diiodomethane on pristine PDMS and (d) diiodomethane on fluorinated PDMS.](image2)

<table>
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<th>Membrane</th>
<th>$\gamma_s$ (mJ/m$^2$)</th>
<th>$\gamma_p^s$ (mJ/m$^2$)</th>
<th>$\gamma_d^s$ (mJ/m$^2$)</th>
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</thead>
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<td>Pristine PDMS</td>
<td>19.36</td>
<td>0.037</td>
<td>19.32</td>
</tr>
<tr>
<td>Fluorinated PDMS</td>
<td>5.31</td>
<td>0.084</td>
<td>5.23</td>
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hydrophobicity is favorable for efficient removal of solvents from water during the pervaporation process [36,44,45]. More importantly, the lipophobicity, which is the unique feature of fluorinated PDMS membrane, would benefit the reduction of molecular interaction between the membrane surface and the microbes in the fermentation broth to suppress the biofouling [46].

3.3. Performance of fermentation-pervaporation coupled process

Pervaporation process can be integrated with fermentation process to in-situ remove the produced solvents to relief the solvent inhibition on the microbial growth in order to realize continuous fermentation with higher productivity. Apparently, the separation performance and anti-biofouling properties of the pervaporation membranes are the key parameters to well establish this fermentation-pervaporation coupled process [47].

In this work, we applied the as-prepared PDMS membranes in the ABE (acetone-butanol-ethanol) fermentation-pervaporation coupled process. The membrane separation performance during the coupled process was shown in Fig. 7. The pristine PDMS membrane separation performance was declined obviously (Fig. 7a). The total flux and ABE separation factor were decreased from 0.80 kg/m$^2$ h and 20.6 to 0.36 kg/m$^2$ h and 7.1, namely in the stable state were 55% and 66% lower than that of in the initial state (Fig. 7c–d), respectively. This result is consistent with our previous work [23,48], suggesting the occurrence of organic bio-foulants (e.g. extra-cellular polymeric substances (EPSs), proteins and microbial flocs) to the membrane [49,50]. The bio-fouling can be clearly observed in the digital photo of the used pristine PDMS membrane (Fig. 8a), which was further confirmed by SEM characterizations. As shown in Fig. 8c, the fouled membrane surface was covered with a fouling layer, in which the microbial cells aggregated with each other and absorbed on the membrane surface probably with the linkage of EPSs. It is confirmed that adhesion is a manifestation of the common attractive force between the pristine PDMS surface and organic bio-foulants from fermentation broth [51]. Compared with the fresh pristine membrane, the performance of the bio-fouled pristine PDMS membrane was almost reversible after water washed. The total flux and ABE separation factor were restored from 0.38 kg/m$^2$ h and 7.1 to 0.78 kg/m$^2$ h and 20.7 that is close its original performance (0.80 kg/m$^2$ h and 20.6). This result is consistent with our previous work [23].

Impressively, the fluorinated PDMS membrane exhibited high and stable separation performance during the continuous solvent removal in the fermentation-pervaporation coupled process. As shown in Fig. 7b, no significant variation in overall separation performance of the fluorinated PDMS membrane was observed in the over 130 h integration process. The total flux and ABE separation factor were stabilized from the initial 0.80 kg/m$^2$ h and 24.5 to 0.73 kg/m$^2$ h and 21.1, respectively. The average total flux and separation factor of fluorinated PDMS membrane were increased by 37% and 104% compared with that of the pristine PDMS membrane. As shown clearly in Fig. 8b and d, after being used in the long coupling process, the fluorinated PDMS membrane was almost not attached by the complex components of fermentation broth, especially the microbes were invisible on the membrane surface. Such excellent separation performance and anti-fouling property should be attributed to the hydrophobic and lipophobic fluorinated PDMS membrane with ultra-low surface energy, thereby minimizing the adhesion of the adsorbents onto the membrane surface and further delaying the membrane fouling [4,46]. That is, the fluorinated membrane showed distinct advantages over the pristine PDMS membrane for the in-situ removal of bio-products in the fermentation-pervaporation coupled process.
The performance of the ABE fermentation after integrating with pervaporation process are shown in Figs. 9–10. Firstly, it should be noted that the fed-batch fermentation process with 11 times successive addition of glucose and ~145 h in total was realized by the integration of PDMS membrane to in-situ remove the produced solvents from the broth. Otherwise, batch fermentation with only single addition of glucose is often used in the conventional ABE fermentation process because the microbial growth was inhibited by the accumulated solvents in the broth.

Fig. 9a–b showed two key indicators of the fermentation process, glucose concentration and optical density (OD), which reflect the activity and growth rate of the microbes in the broth. Compared with pristine PDMS membrane, a lower glucose concentration and higher OD by coupling with the fluorinated PDMS membrane owing to the higher separation performance and anti-fouling property. The removal of the
produced solvents from the fermentation broth was also accelerated as replacing the pristine PDMS membrane with the fluorinated PDMS membrane. As evidenced in Fig. 9c-d, the main product, butanol started to accumulate after fermentation of 60 h although the pristine PDMS membrane was integrated, while the butanol concentration in the fermentation broth kept decreasing after coupling with the fluorinated PDMS membrane. In the fermentation process, ABE concentration was increased with successive addition of glucose. Compared with pristine PDMS membrane, a lower glucose concentration and higher OD by coupling with the fluorinated PDMS membrane owing to the higher separation performance and anti-fouling property. The removal of the produced solvents from the fermentation broth was also accelerated as replacing the pristine PDMS membrane with the fluorinated PDMS membrane.

Fig. 10 compares the ABE concentration in the final fermentation broth and ABE productivity of three fermentation processes: 1) batch fermentation without coupling membrane, 2) fed-batch fermentation coupled with pristine PDMS membrane and 3) fed-batch fermentation coupled with fluorinated PDMS membrane. In the batch fermentation without membrane process, ABE concentration finally reached 18.5 g/L, and ABE productivity was only 0.257 g/L/h due to the inhibition of ABE on the microbial growth. By integrating with PDMS membrane for in-situ solvent removal, the ABE concentration in the broth was significantly reduced as low as 6.0 g/L, thereby leading to the enhancement of ABE productivity as high as 51%. In comparison with the pristine PDMS membrane, the fluorinated PDMS membrane with higher and more stable separation performance extracted much more ABE products from the fermentation process, resulting in a more thorough alleviation of product inhibition and thus higher ABE productivity. Therefore, a more energy-efficient and productive bio-butanol production process can be expected by integrating the fluorinated PDMS membrane.

4. Conclusions

A new kind of anti-biofouling PDMS membrane was fabricated by introducing fluoroalkyl groups to create an ultra-low energy surface. The facile crosslinking reaction between fluorosilane and hydroxyl-terminated PDMS realized a simultaneous achievement of hydrophobicity and lipophobicity in the PDMS membrane. During the application of fermentation-pervaporation coupled process, the fluorinated PDMS membrane exhibited excellent anti-biofouling property, as well as higher and much stable separation performance than the pristine PDMS membrane. The low energy surface built by the fluoroalkyl groups successfully alleviated microbial adhesion onto the membrane and delay the membrane bio-fouling. In the 140 h fed-batch fermentation coupling process, the stabilized total flux and ABE separation factor were enhanced from 0.36 kg/m²h and 7.1 for the pristine PDMS membrane to 0.74 kg/m²h and 21.8 for the fluorinated PDMS membrane, leading to the enhancement of ABE productivity as high as 51% compared with batch fermentation process. The proposed fluorinated PDMS membrane with both anti-biofouling and hydrophobic properties show great potential in application of biofuels production.

Declaration of competing interest

The authors declare no competing financial interest.

CRediT authorship contribution statement

Haipeng Zhu: Investigation, Formal analysis, Writing - original draft, Writing - review & editing. Xinran Li: Investigation. Yang Pan: Investigation. Gongping Liu: Conceptualization, Writing - original draft, Writing - review & editing, Supervision. Hao Wu: Investigation. Min Jiang: Writing - review & editing. Wanqin Jin: Conceptualization, Writing - original draft, Writing - review & editing, Funding acquisition, Supervision.

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