

## PVDF membrane with tea powder adhered for efficient separation of emulsified oil

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**Abstract**—Conventional oily wastewater treatment can remove slick oil and dispersed oil well, but it is difficult for it to remove emulsified oil. Nonetheless, the development of super wetting materials provides a key role in treating the emulsified oil, but there are some problems, such as expensive raw materials, complicated processes, as well as secondary pollution. In order to treat these problems, a brand-new oil/water separation membrane (TEA/PVDF membrane) was developed by combining the viscosity of sodium alginate (SA) and the filter tea powder (TEA) onto the surface of the polyvinylidene fluoride (PVDF) membrane by a vacuum pump. Furthermore, the underwater oleophobic angle reached 135°. Moreover, the oil-water separation experiments of oil-in-water emulsion utilizing TEA/PVDF membrane demonstrated excellent separation efficiency (99.6%) and good flux (254 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>). Notably, upon ten cycles, the oil removal rate was still as high as 99.2%. Moreover, the TEA/PVDF membrane was able to separate oil-in-water emulsions in environments with strong acids, strong bases, and high salt concentrations, with a separation efficiency of over 95.9%. Such a novel oil/water separation membrane is economic, environmentally protective, and simple production process, which exhibits overwhelming potential in practical life for treating oily wastewater.

Keywords: Super Wetting Materials, Tea Powder, PVDF Membrane, Oil-in-water Emulsions, Separation

### INTRODUCTION

Economic globalization has created favorable conditions for the growth of the water transportation industry, and ships play a crucial role as the principal water transportation vehicles [1-3]. Nevertheless, in the process of sailing, unavoidably, a substantial amount of oily sewage is produced. Direct emissions of oil and sewage pollute the environment [4], as well as waste resources. The sources of bilge water on ships include fuel oil, lubricating oil, and water leaking from pipelines. Moreover, the chemical composition of bilge water is complex, with salt concentration ranging from 5 to 30 g/L and pH range from 3 to 10, due to the acidity of marine fuel oil as well as alkalinity of lubricating oil, as well as infiltration of seawater [5]. Oil in sewage can be divided into floating oil, decentralized oil, emulsification, and dissolved oil based on the size of the particle size, and the content of dissolved oil can be disregarded [6]. Conventional oil and sewage treatment methods are predominantly gravity, centrifugal, adsorption, chemical, and biological methods, which can remove floating oil and decentralized oil, and yet they have a poor effect on emulsification oil [7]. This is predominantly due to the amount of emulsification oil being smaller (usually between 100 nm and 1,000 nm) [8-10] and the interface stability is also higher. Consequently, it is critical to discover a technique that can effectively

separate emulsification.

Special wetting materials have been utilized in the field of emulsification oil separation in recent years as a result of their adaptability and wide range of applications. One is a superhydrophobic/superoleophilic membrane, which allows oil to permeate and block water. Nevertheless, due to the high viscosity of oil, it is simple to clog the membrane's pores, resulting in a decrease in flux. One is the superhydrophilic/underwater superoleophobic membrane, which allows water to pass through and block the oil. Since water does not clog the pores of the membrane, it has minimal impact on flux and enhanced reusability, and consequently, it is more popular in the field of oil-in-water emulsion separation [11]. Gao et al. regenerated cellulose and PVA onto polyvinylidene fluoride (PVDF) membrane by a simple and inexpensive method, which had a good oil-water separation efficiency (99.99%) and a good flux (318 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>) and reached a separation efficiency of 99.7% after 30 cycles and 30 minutes ultrasonic treatment [12]. Moreover, Long et al. manufactured porous titanium carbide MXene sheets by "oxidation etching" method and applied carboxyl functionalized surface modification for the purpose of endowing porous MXene sheets with more hydrophilic groups, enhancing the wettability of the membrane. Besides, the membrane indicated high permeability (8,083 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>) in separating the oil-in-water surfactant stabilized emulsions [13]. LI et al. proposed a simple method for the purpose of manufacturing a supramolecular polyurea (PU) hydrogel-coated net that can maintain stable underwater superhydrophobic oiliness. PU hydrogel-coated mesh can be resistant to corrosive environments,

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long-term immersion, and mechanical wear to maintain stable underwater superhydrophobic oil. Consequently, they can exhibit high oil/water separation efficiency (>99 percent) in harsh environments and have stable reusability upon prolonged immersion (3 weeks) [14]. These separation membranes have a relatively good separation efficiency and energy, and yet their widespread application is hampered by their complex processes, high costs, and toxic materials. Hence, the production of a simple, low-cost, and environmentally friendly oil and water separation membrane is more in line with market expectations.

Tea residue, the primary byproduct of tea brewing, is rich in polyphenols. The primary components of tea polyphenols are flavanones, which are rich in hydrophilic carbonyl groups [15]. Meanwhile, the PVDF membrane has chemical corrosion resistance, excellent wear resistance, flexibility, high swelling strength, and impact resistance, which is the ideal material for preparing water treatment membranes [10,16]. Nevertheless, PVDF membrane has high hydrophobicity, and its surface is simple to absorb oil droplets and pollutants, which limits its application in oil-water separation. On this basis, the construction of super hydrophilic and hydrophobic surfaces is considered to be an effective solution to membrane oil pollution. There are two predominant methods for the hydrophilic modification of PVDF membrane [17], in which the first is to deposit hydrophilic substances directly on the membrane surface, and the other is to increase the roughness of the membrane surface. Therefore, the tea powder hydrophilic and oil-phobic membrane was prepared by leaching it onto the PVDF membrane. To improve the times of reuse, the adhesive force between the two was increased by sodium alginate. Besides, the brand-new oil/water separation membrane exhibited excellent emulsified oil separation ability, which could be utilized to work in strong acid, strong base, and high salt environments. Such a novel oil/water separation membrane is economic, environmentally protective, and simple production process, which exhibits overwhelming potential in practical life for treating oily wastewater.

## EXPERIMENTAL SECTION

### 1. Material

Green tea, acquired from Guizhou Wofeng Tea Company, Ltd. Hydrophobic PVDF membrane (22  $\mu\text{m}$  in diameter, 11.34  $\text{cm}^2$ ) was purchased from Haining Dexin Materials Technology Co., Ltd. Diesel, oil was provided by Sinopec Group and peanut oil was provided by Luhua Peanut Oil Co., Ltd. Tannin acid ( $\text{C}_7\text{H}_5\text{O}_4$ , AR), sodium alginate ( $\text{C}_6\text{H}_7\text{NaO}_6$ , AR), aquatic ethanol ( $\text{C}_2\text{H}_6\text{O}$ , AR), as well as cetyltrimethylammonium bromide (CTAB, AR) are purchased from China National Medicine Group.

### 2. Preparation of Tea Powder

The waste tea residue was first soaked in anhydrous ethanol, followed by a 30-minute ultrasonic wash, three rounds of washing in deionized water, and a 12-hour oven drying period at 60 degrees Celsius. The dried tea residue was taken out, crushed with a crusher, and fine-screened with a 200 mesh sieve to obtain tea powder.

### 3. Preparation of TEA/PVDF Membrane

As shown in Fig. 1, sonicate the PVDF membrane in absolute ethanol and deionized water for 2 minutes to clean surface impu-



Fig. 1. Illustration of the preparation processes of TEA/PVDF membrane and its application for emulsion separation.

rities. Take 0.2 g of tannic acid and put it into 20 ml of deionized water. For standby, immerse the PVDF membrane in this solution for 10 minutes after thoroughly stirring it. Tannic acid has a large number of phenol groups, which can enhance the hydrophilicity of the PVDF membrane. Then put 0.3 g sodium alginate into 30 ml deionized water, and stir it magnetically for 30 minutes to prepare a uniform solution. Add 3 ml of sodium alginate solution and 0.2 g of tea powder to 40 ml of derived water at the same time. Magnetic stirring for 30 minutes forms a uniform suspension. (0, 6, 9, 12, 15, 18) ml suspension is filtered into PVDF membrane by vacuum pump, and TEA/PVDF membranes of distinct thicknesses are prepared, labeled as  $M_0$ ,  $M_3$ ,  $M_6$ ,  $M_9$ ,  $M_{12}$ , and  $M_{18}$ , respectively. The membranes are then left at room temperature until they are completely dry and ready for use.

### 4. Preparation of Emulsification Oil

0.015 g of CTAB and 0.3 g of oil are added to 150 ml of water, and magnetic stirring is performed at a speed of 2,000 r/min for 2 h to obtain a series of emulsified oils with stable surface activity, which are engine oil-in-water (E/W), diesel-in-water (D/W), as well as peanut oil-in-water (P/W).

### 5. Separation of Emulsification Oil

First clamp the TEA/PVDF membrane with a Buchner suction filtration device fixed with duck nose pliers, and subsequently, pour a specific quantity of emulsified oil and apply a negative pressure of 0.08 Mpa. Moreover, they collect the filtered liquid and record the time required. And the separation efficiency and flux of oil in water lotion are calculated by formula (1) and (2) respectively:

$$R = \left(1 - \frac{C_0}{C_1}\right) \times 100\% \quad (1)$$

$$J = \frac{V}{A \cdot P \cdot t} \quad (2)$$

The separation efficiency is  $R$  (100%),  $c_0$  is the oil concentration in the filtrate after separation, and  $c_1$  is the oil concentration in the oil-water mixture before separation.  $J$  ( $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ ) is the membrane permeability,  $V$  (L) is the filtered solution volume,  $A$  ( $\text{m}^2$ ) serves as the effective separation area, and  $P$  (bar) represents the

operating pressure,  $t$  (h) is the separation time.

## 6. Characterization

Use Fourier infrared spectrometer (FTIR, WQF520 model) to detect and analyze the sample; use X-ray diffraction (XRD) measuring instrument (AXS D8 company Advance type) to characterize the crystal structure of distinct membranes; utilize scanning electron microscope (SEM, Fei Quanta 650 FEG model) to observe the surface shape and morphological structure of the PVDF membrane before and after the modification. At room temperature, drop liquid drops of a specific size onto the membrane, and then use a VGA industrial camera to analyze the hydrophilic angle (WCA) and the underwater oil repellent angle (UOCA) of the membrane; use software Nano Measurer 1.2 to analyze the diameter distribution of the membrane.

## RESULTS AND DISCUSSION

### 1. Characterization and Analysis

Scanning electron microscopy was utilized to observe the surface and side morphology, and the results are demonstrated in Fig. 2(a). The surface of the original PVDF membrane is smooth and flat. The higher resolution image in the upper right corner reveals pores with an average pore size of 450 nm that are densely packed [18]. Fig. 2(b) is the surface diagram of the TEA/PVD membrane. There are numerous small particles of nanoparticles piled up together in a disorderly manner, and there are gaps and uneven spac-

ing between particles. It is evident that from the macroscopic figure in the upper right corner, these particles have the general appearance of an irregular honeycomb with a distinct tubular structure. The pipe diameter distribution is indicated in Fig. 2(d), and the average pipe diameter is 55 nm. It is these micro-nano pipes that provide an effective channel for the separation of oil emulsion [19]. Additionally, the surface is rougher than that of Fig. 2(a), and this structure is one of the necessary conditions for hydrophilic materials [20]. Fig. 2(c) is a cross-section of the TEA/PVD membrane; its thickness is approximately three times that of the previous membrane, making it rougher and more conducive to hydrophilic demulsification.

The ATR-FTIR spectra (Fig. 2(e)) of the original PVDF indicate characteristic peaks at  $760\text{ cm}^{-1}$ ,  $890\text{ cm}^{-1}$ , and  $990\text{ cm}^{-1}$ , respectively, which are attributed to the tensile vibration of the  $-\text{CH}_2$  functional group in the benzene ring. The characteristic peaks at  $1,100\text{ cm}^{-1}$ ,  $1,200\text{ cm}^{-1}$  as well as  $1,400\text{ cm}^{-1}$  are all triggered by the stretching vibration of the  $-\text{CF}_2$  bond, and the bending vibration at  $1,600\text{ cm}^{-1}$  is brought about by the  $\text{C}=\text{C}$  bond on the benzene ring [21], which is all inherent properties of PVDF membrane. On the condition that the suspension of tea powder and sodium alginate precipitated on the PVDF membrane, three new characteristic peaks of  $1,750\text{ cm}^{-1}$ ,  $2,900\text{ cm}^{-1}$ , and  $1,750\text{ cm}^{-1}$  were caused by the stretching vibration of the  $\text{C}=\text{O}$  bond [22]; carbonyl group is an essential component of tea polyphenols. The bimodal peak near  $2,900\text{ cm}^{-1}$  is a stretching vibration of the  $-\text{CH}_3$  functional group, which may

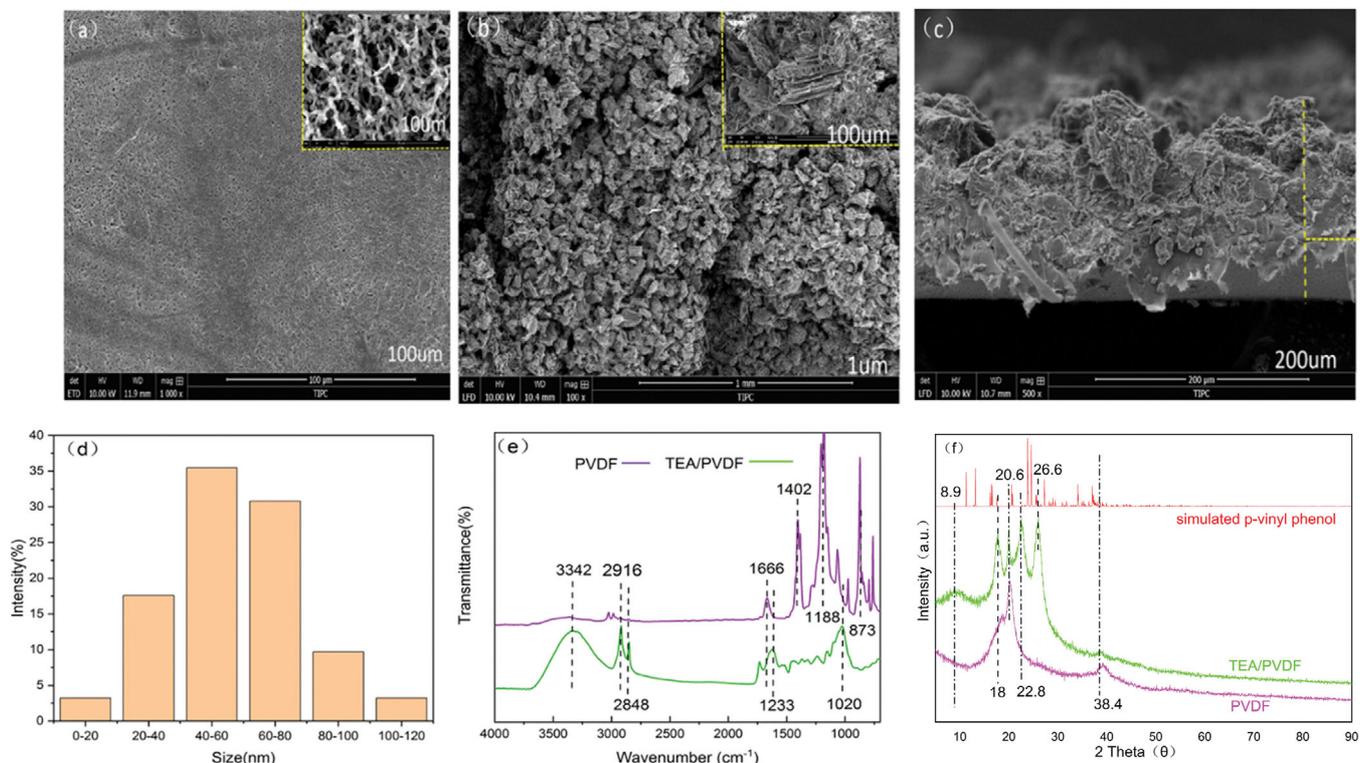


Fig. 2. FE-SEM images of (a) the initial PVDF membrane and (b) the TEA/PVDF membrane and the (c) Cross-section of images of the TEA/PVDF membrane surface. (d) Distribution of pore size in TEA/PVDF membrane. (e) FT-IR spectra of the initial PVDF membrane and the TEA/PVDF membrane. (f) XRD analysis of the initial PVDF membrane, the TEA/PVDF membrane, and the simulated p-vinyl phenol.

be the residue of ethanol cleaning PVDF membrane, and has no major influence on experimental results. Moreover, the  $3,300\text{ cm}^{-1}$  is the contraction vibration of the  $-\text{OH}$  functional group, which may be from tea polyphenols or sodium alginate. All of the preceding data indicated that the tea powder successfully adhered to the PVDF membrane using sodium alginate.

The XRD analysis (Fig. 2(f)) indicates that the original PVDF membrane only has a sharp characteristic peak at  $20.6^\circ$ , which is the characteristic diffraction peak of  $\beta$ -crystal in the PVDF molecular structure, correlated with the mixed crystal plane of 110 and (200), and this peak persists within the composite membrane [23]. During the filtration of tea powder and alginate solution through a PVDF composite membrane, the molecular structure of PVDF remained intact and no obvious damage occurred, according to the results. The characteristic peaks of the new composite membrane appeared at  $18.0^\circ$ ,  $22.8^\circ$  and  $38.4^\circ$ . In comparison with the standard cards, notably, it is p-vinyl phenol, which has a large number of carbonyl and phenol groups and could enhance the hydrophilicity of the composite membrane. The XRD of simulated p-vinyl phenol corroborates the measured data (Fig. 2(f)). Two new characteristic peaks appeared in  $8.9^\circ$  and  $26.6^\circ$ , methyl protocatechuate, an essential component of tea powder, indicating once more that tea powder adhered successfully to PVDF membrane.

## 2. Surface Wettability Property

The superhydrophobic and superoleophobic substances forcibly absorb the water molecules in the emulsion through their hydro-

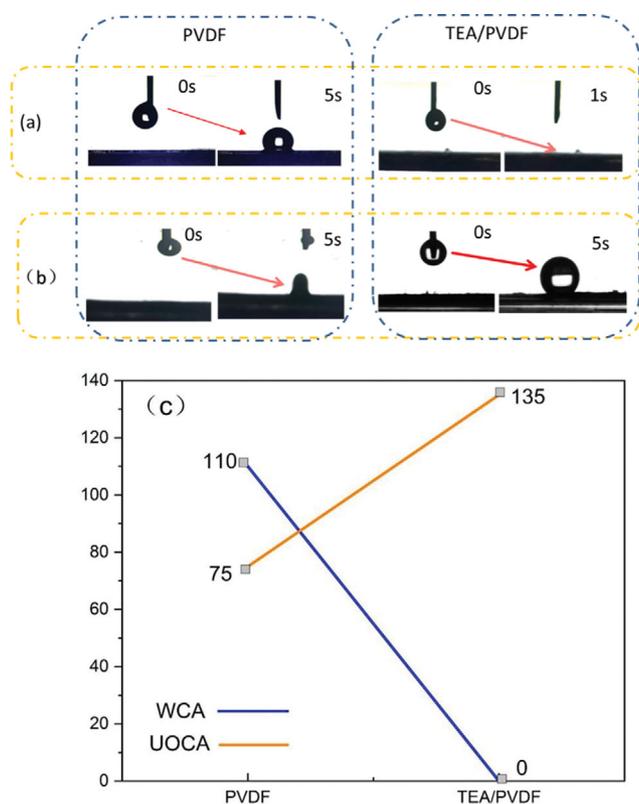


Fig. 3. (a) WCA picture of PVDF after 5 s and WCA picture of TEA/PVDF after 1 s. (b) After 5 s, UOCA picture of PVDF and TEA/PVDF. (c) WCA and UOCA of PVDF and TEA/PVDF.

philicity; oil-water separation is accomplished by leaving the oil molecules intact. Consequently, the hydrophilic and oleophobic properties of the separation membrane contribute significantly to the success of demulsification [24]. As illustrated in Fig. 3(a), the PVDF membrane changed from hydrophobic to hydrophilic after being modified by tea powder, and its WCA in the air (Fig. 3(c)) changed from  $105^\circ$  to  $0^\circ$ , indicating that the membrane transformed from hydrophobic to extremely hydrophilic. Meanwhile, it is evident from Fig. 3(b) that the membrane changes from slightly oil-philic to superoleophobic, and the UOCA (Fig. 3(c)) changes from  $75^\circ$  to  $135^\circ$ . The above results demonstrate that the hydrophilic as well as oleophobic modification of the membrane is very successful.

## 3. Chemical Stability

Soak the TEA/PVDF membrane in the water solution with pH 3-12, and test its contact angle after 6, 12, 18, and 24 hours, correspondingly. The results indicate that the WCA of the TEA/PVDF membrane is frequently 0, while UOCA is mostly above  $127^\circ$  (Fig. 4(a)).

Soak the TEA/PVDF membrane in the water solution with a salt concentration of 5.0-35.0 g/L, and test its contact angle after 6, 12, 18, and 24 hours. The results display that the WCA of the TEA/

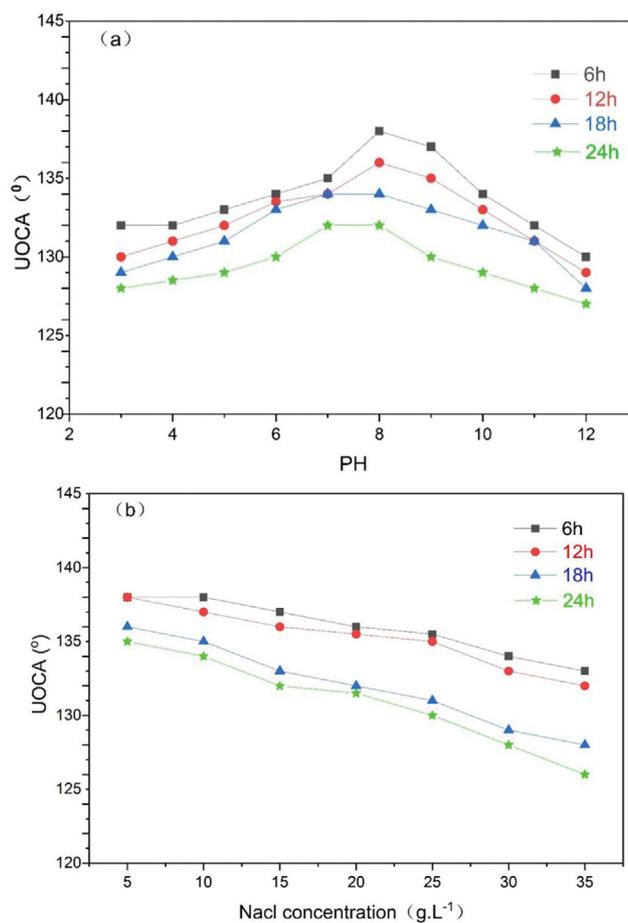


Fig. 4. (a) UOCA at different PH after TEA/PVDF membrane immersion for (6, 12, 18, 24) hours. (b) UOCA at different salt concentrations upon TEA/PVDF membrane immersion for (6, 12, 18, 24) hours.

PVDF membrane is frequently 0, while UOCA is mostly above  $126^\circ$  (Fig. 4(b)).

This illustrates that TEA/PVDF membrane can maintain its super hydrophilic and underwater super oil hydrophobic properties under harsh conditions, which is extremely significant for practical applications.

#### 4. Oil/Water Separation Property

For the purpose of verifying the oil-water separation ability of the TEA/PVDF filtration membrane, we conducted an oil-water separation test on the E/W. The results illustrated that the flux of the original PVDF membrane reached  $1,875 \text{ (L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1})$ , and

yet it could hardly trap the oil, and the efficiency of separation was only 26.3%. The separation efficiency increased considerably as more suspensions were pumped to the PVDF, from 87.5% initially to 100% later. Though, at the same time, the flux decreased substantially, from  $952 \text{ (L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1})$  to  $58 \text{ (L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1})$  (Fig. S1). To consider both separation efficiency and flux, the separation membrane  $M_{12}$  was selected as the sample for experimentation. Its initial separation showed a separation efficiency of 99.9% and a flux of  $254 \text{ (L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1})$ . Prior to separation, it is a milky white turbid fluid, and after separation, the filtrate is extremely clear (Movie S1). The pre-separation and post-separation images of the oil emul-

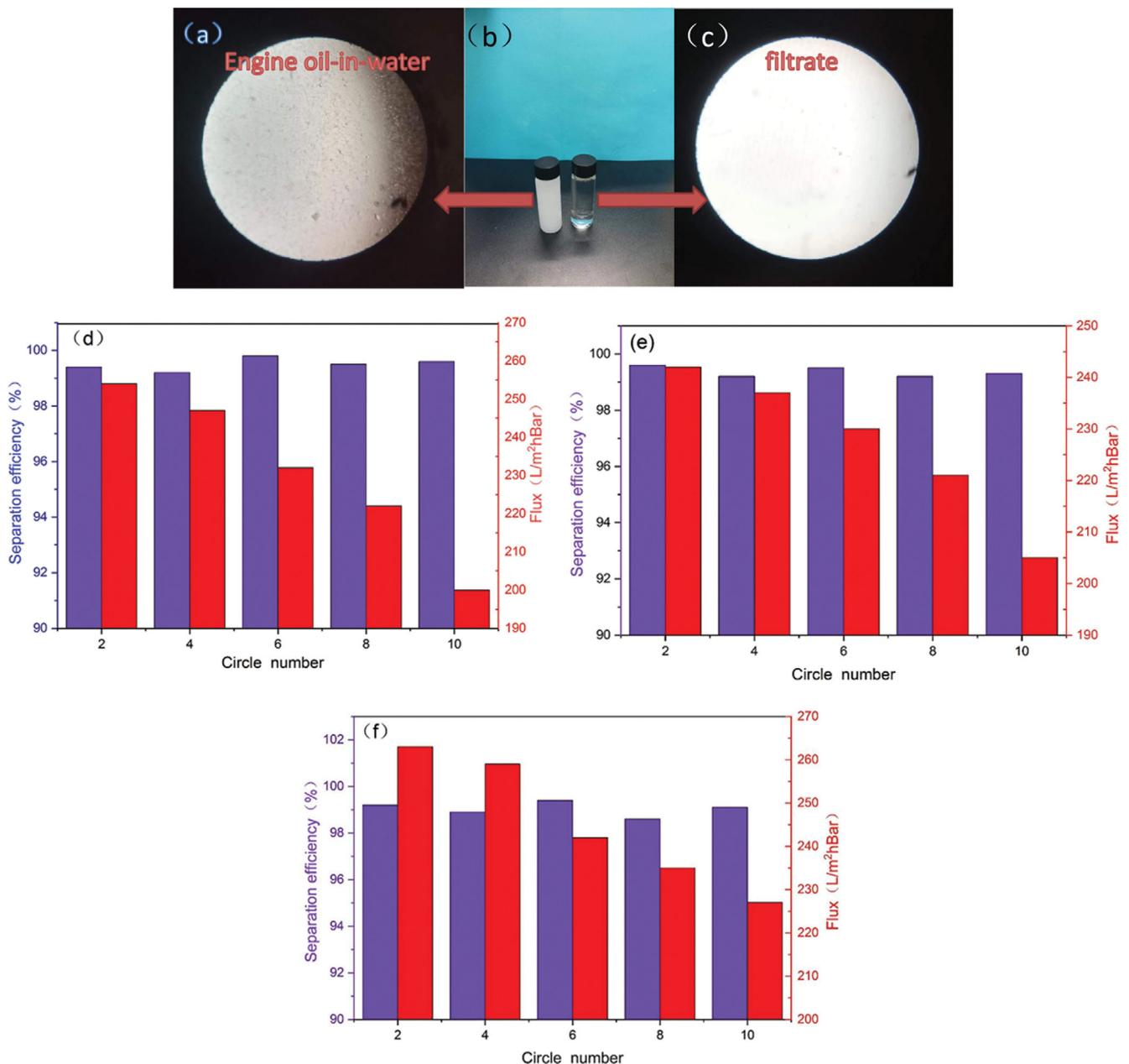


Fig. 5. ((a) and (c)) The optical microscopy images and (b) the digital images of the engine oil-in-water emulsions before and after separation. (d) Separation efficiency and flux of E/W emulsions. (e) Separation efficiency and flux of D/W emulsions. (f) Separation efficiency and flux of P/W emulsions.

**Table 1. Comparison of various materials used to separate oil-in-water emulsions**

Materials	Separation type of oil	Using toxic substance	Corrosion resistance	Separation efficiency (%)	Permeating flux ( $L m^{-2} h^{-1}$ )	Reference
Cellulose-TA-PV A-PVDF membrane	Oil-in-water emulsions	yes	no	99.99	318	[10]
ESP-Coated PVDF Membrane	Oil-in-water emulsions	no	no	99.6	229	[15]
SnO <sub>2</sub> coating	Oil-in-water emulsions	no	no	97.11	200	[20]
Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> mineral coating on PVDF membrane	Oil-in-water emulsion	yes	no	99.6	1,000	[22]
Magnetic polyurethane sponge	Oil-water	no	no	98.9	none	[25]
TEA/PVDF membrane	Oil-in-water emulsion	no	yes	99.9	257	this work

Abbreviation: none, not measured.

sion (Fig. 5(a)-(c)) were observed with a microscope and it was discovered that the dense microscopic oil droplets prior to separation were no longer present after separation [25]. To verify the recyclability of the TEA/PVDF filtration membrane, the oil-water separation was repeated ten times and only water was used to clean the separation membrane after each separation [26]. The results are in Fig. 4(d). During the whole separation process, the separation efficiency remained above 99.2%, which signifies that the separation membrane has a high capacity for recycling. In addition, the flow rate in the whole separation process is almost kept above 200 ( $L m^{-2} h^{-1} bar^{-1}$ ), indicating that the TEA/PVDF filtration membrane has good anti-fouling performance. Fig. 4(e) and 4(f) demonstrate that satisfactory results are also obtained when D/W and P/W are separated ten times to verify the diversity of the composite membrane. Consequently, the separation performance of the prepared membranes has a marked enhancement over previous works as displayed in Table 1.

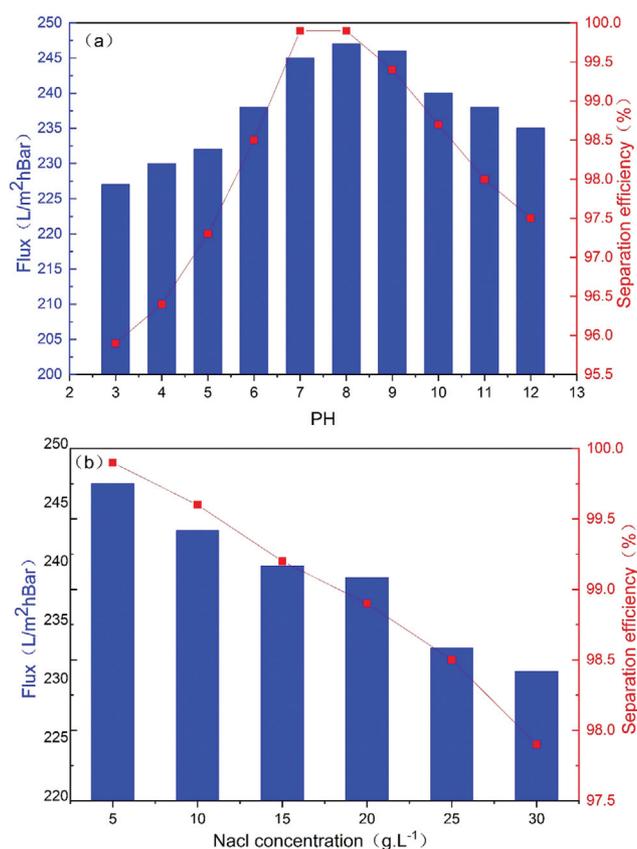
#### 4-1. Effect of pH on the Separation Performance of Oil and Water

TEA/PVDF membranes are used to conduct oil-water separation experiments on oil-water mixtures at different pH values, and the separation efficiencies (R) and flux (J) of the membrane are calculated. Fig. 6(a) demonstrates the outcomes.

As can be seen, when pH is less than 8, separation efficiency and membrane flux increase with increasing pH: when pH is higher than 8, the separation efficiency and flux of the membrane decrease with the increase in pH. When pH is 3, the separation efficiency is 95.9% and the flux is 227 ( $L m^{-2} h^{-1} bar^{-1}$ ). When pH is 8, the separation efficiency and flux reach the maximum of 99.9% and 247 ( $L m^{-2} h^{-1} bar^{-1}$ ). Under acidic conditions, the separation efficiency and flux of the membrane are lower. The primary reason for this phenomenon is that strong acidity and strong alkalinity corrode the membrane surface, thereby reduce the membrane's roughness and hydrophilicity as well as underwater oiliness [27]. The decrease in hydrophilicity will reduce the demulsification ability of the membrane, and the decrease in underwater oil phobia will increase the probability of oil blocking the membrane pores. Hence, in strong acid or alkali environment, membrane separation of emulsified oil efficiency and flux will be lowered [28].

#### 4-2. Effect of Salt Concentration on the Separation Performance of Oil and Water

TEA/PVDF membranes are employed to conduct oil-water separation experiments on oil-water mixtures with distinct salt concen-



**Fig. 6. (a) Flux and efficiency at distinct PH values. (b) Flux and efficiency at distinct salt concentrations.**

trations, and the separation efficiency (R) and flux (J) of the membrane are calculated. Fig. 6(b) demonstrates the outcomes.

As can be seen, on the condition that salt concentration increases, the separation efficiency and flux decrease. Moreover, on the condition that the salt concentration is 5 g/L, the separation efficiency is 99.8%, and the flux is 247 ( $L m^{-2} h^{-1} bar^{-1}$ ). Additionally, when the salt concentration was increased to 30 g/L, the separation efficiency was 97.9%, and the flux was 231 ( $L m^{-2} h^{-1} bar^{-1}$ ). Thus, when the salt concentration increased from 5 g/L to 30 g/L, the separation efficiency decreased by 1.9%, and the flux of the membrane decreased by 16 ( $L m^{-2} h^{-1} bar^{-1}$ ). The salt concentration has little effect on the membrane's separation efficiency and flux over-

all. Besides, as an anionic polyelectrolyte, sodium alginate is easily affected by electrolytes in the solution, which may explain this phenomenon. After the NaCl solution is added, the surface force of sodium alginate on the tea powder decreases, which will cause the tea powder to fall off and decimate the membrane's structure, resulting in lower separation efficiency [29]. At the same time, the addition of NaCl increases the concentration on the oil emulsion side of the separation membrane, whereas on the opposite side of the separation membrane, where water is the primary constituent, the concentration is essentially unchanged [30]. Consequently, the osmotic pressure goes down, which contributes to a decrease in flux.

### MECHANISM ANALYSIS

To better illustrate the mechanism of oil-water separation in the filter membrane, a model was developed in Fig. 7(a). The oil in emulsified oil is stable and does not rise or accumulate [31]. Nevertheless, when a negative pressure of 0.08 Mpa is applied below the filter membrane, the emulsified oil will be forced to flow to the filter membrane due to the action of atmospheric pressure. At the moment on the condition that the oil emulsion touches the filter membrane, due to the hydrophilicity of the filter membrane, the water in the oil emulsion will be quickly sucked by the filter membrane to form a stable solid-liquid layer for the purpose of preventing the proximity of the oil droplets [32]. The emulsified oil is successfully demulsified in this manner. Small water molecules then pass through the filter membrane's pores to separate the oil from the water.

Even when subjected to external vibration and other adverse conditions, the membrane maintains its separation efficiency. It is assumed that the stable layer formed by the membrane and water is disrupted by the vibration and that the demulsified oil comes into direct contact with the membrane (Fig. 7(b)). Nevertheless, the average pore size of the filter membrane is only 55 nm, which is much smaller than the oil droplet particle size. Additionally, it is super oil-phobic underwater, which makes it challenging for the oil droplet to pass through the membrane.

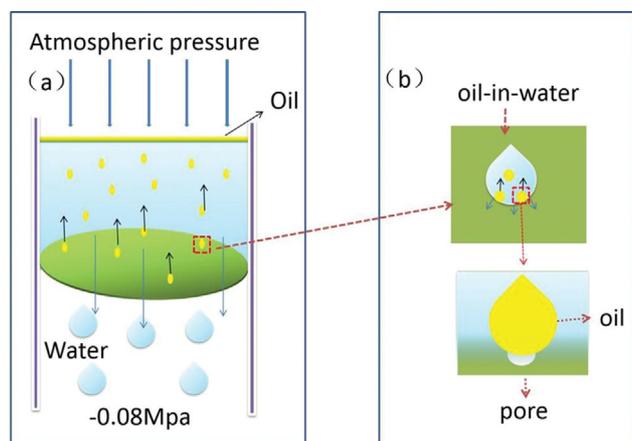


Fig. 7. Schematic diagram of separation mechanism of oil-in-water emulsion system under normal (a) and extreme conditions (b).

### CONCLUSIONS

Natural plant tea powder and sodium alginate were adhered to the surface of the PVDF membrane by a deposition method, which enhanced the surface roughness and wettability of the membrane, and prepared a new superhydrophobic/underwater superhydrophobic composite membrane. Furthermore, the advantage of the composite membrane is that it is composed of waste and does not cause secondary environmental contamination. In comparison with the PVDF membrane, the separation performance and repeatability of the prepared composite membrane are substantially enhanced in the treatment of various oil-in-water emulsions; the separation efficiency was up to 99.9%, and the oil-water emulsion membrane flux was as high as  $247 \text{ (L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}\text{)}$ . The results indicate that the composite membrane prepared in this paper possesses promising application potential in oil-water separation and can provide a feasible concept for the treatment of oil-bearing industrial wastewater by membrane technology.

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### DATA AVAILABILITY

No data was used for the research described in the paper.

### DECLARATION OF COMPETING INTEREST

The authors declare that they have no recognized competing financial interests or personal relationships that could be perceived as having influenced the work described in this paper.

### CRediT AUTHORSHIP CONTRIBUTION STATEMENT

**Junshuang Zhang:** Conceptualization, Methodology, Investigation, Writing - original draft. **Yue Wu:** Writing - review & editing. **Mengsheng Xia:** Writing - review & editing. **Qijiang Yang:** Writing - review & editing. **Qinyao Xu:** Writing - review & editing. **Wenwen Feng:** Resources, Supervision, Project administration.

**Ethical approval** (Not Applicable)

### SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

### REFERENCES

1. S. Wan, X. Yang, X. Chen, Z. Qu, C. An, B. Zhang, K. Lee and H. J. J. o. C. P. Bi, *J. Clean. Prod.*, **376**, 134266 (2022).
2. M. M. Ali, M. S. Islam, A. R. M. T. Islam, M. S. Bhuyan, A. S. Ahmed, M. Z. Rahman and M. M. Rahman, *Mar. Pollut. Bull.*, **175**, 113274 (2022).

3. B. Kamal and S. Kutay, *Ocean Coastal Manag.*, **215**, 105939 (2021).
4. J. Gao, J. Wang, M. Cai, Q. Xu, J. Zhang, X. Cao, J. Zhang and Y. Chen, *Carbohydr. Polym.*, **300**, 120242 (2022).
5. J. Zhang, F. Zhang, W. Fang and J. Jin, *J. Membr. Sci.*, **672**, 121472 (2023).
6. Y. Chen, H. Liu, M. Xia, M. Cai, Z. Nie and J. Gao, *Sci. Total Environ.*, **856**, 159271 (2023).
7. J. Gao, M. Cai, Z. Nie, J. Zhang and Y. Chen, *Sep. Purif. Technol.*, **275**, 119174 (2021).
8. X. Wang, M. Li, Y. Shen, Y. Yang, H. Feng and J. Li, *Green Chem.*, **21**, 3190 (2019).
9. M. Wu, P. Mu, B. Li, Q. Wang, Y. Yang and J. Li, *Sep. Purif. Technol.*, **248**, 117028 (2020).
10. G. Shi, Y. Shen, P. Mu, Q. Wang, Y. Yang, S. Ma and J. Li, *Green Chem.*, **22**, 1345 (2020).
11. E. Moon, E. Kang, W. Song, B. J. Kim, H. J. Cha and Y. S. Choi, *Korean J. Chem. Eng.*, **40**, 405 (2023).
12. J. Gao, J. Wang, Q. Xu, S. Wu and Y. Chen, *Green Chem.*, **23**, 5633 (2021).
13. T. T. Loc, N. D. Dat and H. N. Tran, *Korean J. Chem. Eng.*, **38**, 2 (2022).
14. B. Li, C. Wang, X. Tian, Y. Luo, X. Cao and Z. Luo, *Colloids Surf. A: Physicochem. Eng. Asp.*, **654**, 130085 (2022).
15. J. Li, Y. Wang and J. H. Suh, *Food Sci. Hum. Wellness*, **11**, 524 (2022).
16. U. Baig, M. Dastageer and M. Gondal, *Colloids Surf. A: Physicochem. Eng. Asp.*, **660**, 130793 (2023).
17. L. Lu, W. Ding, J. Liu and B. Yang, *Nano Energy*, **78**, 105251 (2020).
18. H. Zhang, Y. Shen, M. Li, G. Zhu, H. Feng and J. Li, *ACS Sust. Chem. Eng.*, **7**, 10880 (2019).
19. Y. Shi, Y. Hu, J. Shen and S. Guo, *J. Membr. Sci.*, **629**, 119294 (2021).
20. X. Zhu, L. Zhu, H. Li, C. Zhang, J. Xue, R. Wang, X. Qiao and Q. J. O. M. S. Xue, *J. Membr. Sci.*, **630**, 119324 (2021).
21. C. Xu, F. Yan, M. Wang, H. Yan, Z. Cui, J. Li and B. He, *J. Membr. Sci.*, **602**, 117974 (2020).
22. T. Otitoju, A. Ahmad and B. Ooi, *J. Water Process Eng.*, **14**, 41 (2016).
23. H.-C. Yang, Y. Xie, H. Chan, B. Narayanan, L. Chen, R. Z. Waldman, S. K. Sankaranarayanan, J. W. Elam and S. B. J. A. n. Darling, *ACS Nano*, **12**, 8678 (2018).
24. D. Parbat, A. Das, K. Maji and U. J. o. M. C. A. Manna, *J. Mater. Chem. A*, **8**, 97 (2020).
25. L. Yan, X. Yang, Y. Zhao, Y. Wu, R. M. Moutloali, B. B. Mamba, P. Sorokin and L. Shao, *Sep. Purif. Technol.*, **285**, 120383 (2022).
26. X. Lv, X. Li, L. Huang, S. Ding, Y. Lv and J. Zhang, *Korean J. Chem. Eng.*, **39**, 475 (2022).
27. B. Porkar, P. A. Atmianlu, M. Mahdavi, M. Baghdadi, H. Farimani-iraad and M. A. Abdoli, *Korean J. Chem. Eng.*, **40**, 892 (2023).
28. U. Baig, A. Waheed and M. Dastageer, *J. Environ. Chem. Eng.*, **11**, 109357 (2023).
29. W. Xie, K. Zhao, L. Xu, N. Gao, H. Zhao, Z. Gong, L. Yu and J. Jiang, *Chin. Chem. Lett.*, **33**, 1951 (2022).
30. Z. Panahi and M. Mohsenzadeh, *Int. J. Food Microbiol.*, **380**, 109883 (2022).
31. R. Qu, X. Li, Y. Wei and L. Feng, *Appl. Surf. Sci.*, **532**, 147350 (2020).
32. S. Zhang, S. Chen, H. Li, X. Lai and X. Zeng, *J. Environ. Chem. Eng.*, **10**, 107580 (2022).

## Supporting Information

### PVDF membrane with tea powder adhered for efficient separation of emulsified oil

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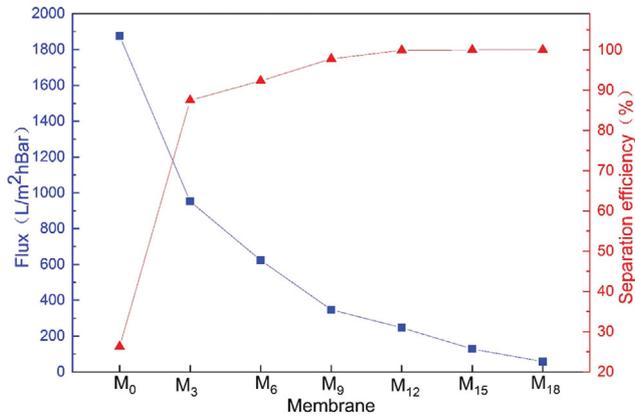


Fig. S1. Separation efficiency and flux of membranes of different thicknesses.