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Preparation of a main-chain-type polybenzoxazine-modified melamine sponge via non-solvent-induced phase inversion for oil absorption and very-high-flux separation of water-in-oil emulsions

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ABSTRACT

Cost-effective, high-performance materials for the removal of oil contamination from water, specifically oil/water emulsions, in an environmentally friendly way are urgently required, but their development remains a major challenge. In this study, a facile water-based non-solvent-induced phase inversion method was applied to fabricate main-chain-type polybenzoxazine-modified melamine sponge (PBZMS). The as-prepared PBZMS possesses superhydrophobicity and superoleophilicity and can remove oil/organic solvents from the surface of water, as well as underwater. PBZMS has an outstanding absorption capacity (up to 170 times its weight), and, after long-term immersion tests in organic solvents, PBZMS maintained its superhydrophobicity. By compressing the PBZMS sponge, we achieved excellent oil–water separation of surfactant-stabilized water-in-oil emulsions (SWOEs) at very high permeation fluxes of 13,900 ± 300 L m^{-2} h^{-1} and 1,353,000 ± 27,700 L m^{-2} h^{-1} bar^{-1} via gravity-driven and pressure-driven (0.025 bar) processes, respectively, yielding an oil purity ≥99.96 wt%. The excellent absorption capacities for various organic solvents and oils, outstanding separation performance for emulsions, stability in harsh chemical environments, and recyclability of PBZMS make it a promising candidate for large-scale applications.

1. Introduction

As a result of the rapid development of various industries, oil spills, water pollution, and environmental problems have increased. The petroleum industry is responsible for many of these contamination incidents, and oil spillage during mining, transportation, and storage are the primary sources of oily wastewater emissions [1–3]. Many efforts have been made to overcome these problems, such as the development of conventional separation methods, including flotation, burning, centrifugation, and settling methods, but these are limited by high operation costs and low separation efficiencies [4]. Therefore, it is imperative to find an appropriate way to solve this worldwide challenge.

In recent years, superwetting materials having exceptional water repellence have been introduced for automotive, marine, and medical applications [5]. Because of their selective superwetting/superantiwetting properties towards oil and water, superwetting materials have been used for the separation of heterogeneous oil–water mixtures and emulsions [6–10]. For the separation of various oil–water mixtures, 3D porous superhydrophobic materials have advantages over their 2D counterparts; for example, large surface areas and volume capacities, better physical strength, better ability to achieve high permeation fluxes, better antifouling properties, and lower energy requirements, which arise because of the easy flow of permeate liquids through the porous structure [11,12]. The most commonly and widely used 3D interfacial superwetting absorbent–separation materials are foams, aerogels, and sponges having high porosities and tunable pore

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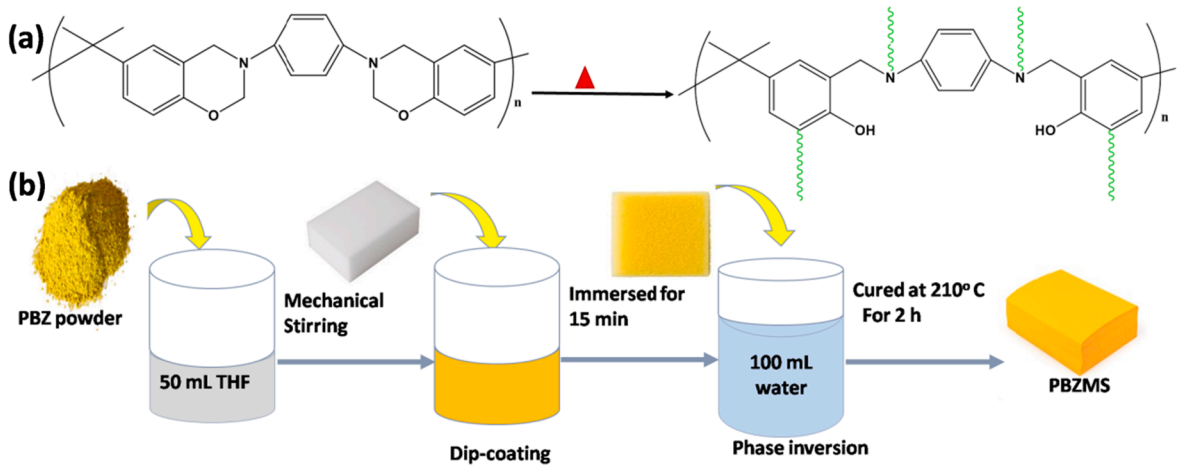

Fig. 1. Schematic illustration of the (a) thermal cross-linking of P(B-pd) and (b) scheme for PBZMS preparation via non-solvent-induced phase inversion.

structures, which are regarded as effective media to remove oil selectively at a high absorption rate [1]. Recently, studies have focused on producing various types of superhydrophobic/superoleophilic sponge-like materials that are efficient in separating surfactant-stabilized water-in-oil emulsions (SWOEs). Wang and coworkers prepared various superhydrophobic/superoleophilic materials using a phase inversion method for the separation of various oil/water mixtures including SWOEs [13]. Liu and coworkers fabricated a broadly applicable and highly efficient superhydrophobic sponge from magnetic polydopamine and branched polydimethylsiloxane via dopamine-mediated surface-initiated atom transfer radical polymerization for the separation of surfactant-stabilized oil-in-water and water-in-oil emulsions [14]. Li et al. fabricated a facile water-based non-fluorinated superhydrophobic sponge for the efficient separation of heterogeneous oil/water mixtures and water-in-oil emulsions [15]. Li et al. prepared a robust porous polydivinylbenzene–polydimethylsiloxane-coated superhydrophobic melamine sponge for the separation of complex oil/water mixtures [16]. However, regardless of their separation abilities for SWOEs, these materials have limitations, for example, the inability to separate SWOEs at high fluxes and efficiencies because of the large pore sizes compared to the small emulsion droplets, incorporation of costly chemicals/materials, complex synthesis, and use of toxic chemicals, including fluorine and nanoparticles, and organic solvents, such as ethanol and acetone, during coating preparation [17]. Therefore, the development of cost-effective, safe, friendly, and durable superhydrophobic/superoleophilic materials through a simple method for the separation of SWOEs at high fluxes and with high efficiencies remains necessary.

In this study, a facile non-solvent-induced phase inversion method was applied to fabricate main-chain-type polybenzoxazine-modified melamine sponge (PBZMS). The as-prepared PBZMS possesses both superoleophilicity and superhydrophobicity and maintains its superhydrophobic property after long-term immersion in organic solvents and other chemical environments. The sample was prepared without incorporating halogens or other inorganic additives and exhibited outstanding absorption capacities for various organic solvents and oils: 62–170 g/g. Further, by compressing the PBZMS sponge, we achieved outstanding oil/water separation performance, having very high permeation flux values for SWOEs of up to 13,900 ± 290 L m^{-2} h^{-1} and 1,353,000 ± 27,700 L m^{-2} h^{-1} bar^{-1} using gravity-driven and pressure-driven (0.025 bar) processes, respectively, and yielding a minimum oil purity of 99.96 wt%. The extraordinary performance of PBZMS for the absorption of organic contaminants and the separation of water-in-oil emulsions indicate its potential for fuel purification and the treatment of industrial discharge.

2. Experimental

2.1. Materials

Commercial melamine sponge (MS) was purchased from BASF (Berlin, Germany). Petroleum ether (60/80) and n-hexadecane (99%) were purchased from Alfa Aesar (Lancashire, UK). Toluene (99.8%) was purchased from Sigma-Aldrich Corp. (St. Louis, Missouri, USA). Chloroform (99%) and dichloromethane (>99%) were purchased from Fluka^{TR} (Seelze, Germany). Span 80 and n-octane (98%) were purchased from Acros Organics (Geel, Belgium). Isooctane (99.7%), n-hexane (95%), and tetrahydrofuran (99.0%) were purchased from TEDIA Company Inc. (Fairfield, USA). 4,4′-Isopropylidenediphenol and paraformaldehyde were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). 1,4-Phenylenediamine was purchased from Chriskev Inc. (Kansas, USA).

2.2. Preparation of main-chain-type polybenzoxazine-modified melamine sponge

The main-chain-type polybenzoxazine precursor P(B-pd) was prepared according to our previous report [18]. PBZMS was prepared using non-solvent-induced phase inversion method. Initially, a coating solution was prepared by mixing 1.5 g P(B-pd) in 50 mL of THF, then the solution was further filtered using polytetrafluoroethene (PTFE) syringe filter (0.2 μm). The MS was dunked into the prepared coating solution till saturation and followed by the removal of the residual mixture with a squeezing process. Consequently, the coated MS was immersed in a water container for 15 min to undergo phase inversion, and then squeezed, rinsed in ethanol and DI water, respectively, to remove any unwanted residual mixtures. After drying at 100 °C for 1 h, the resulting substrate was cured in oven (210 °C, 2 h).

2.3. Preparation of surfactant-stabilized water-in-oil emulsions

Each SWOEs was prepared in the same fashion to our previous work [19]. Firstly, span 80 (0.3 g) was added into 98 mL of different types of oils/organic solvents (n-hexane, toluene, n-octane, isooctane, gasoline, n-hexadecane, and petroleum ether) followed by adding 2 mL of DI water drop-by-drop while vigorously agitating. Stirring the mixtures continued until the stable milky solutions were obtained. All the prepared emulsions exhibited high stabilities and were stable for more than 168 h without apparent phase separation.

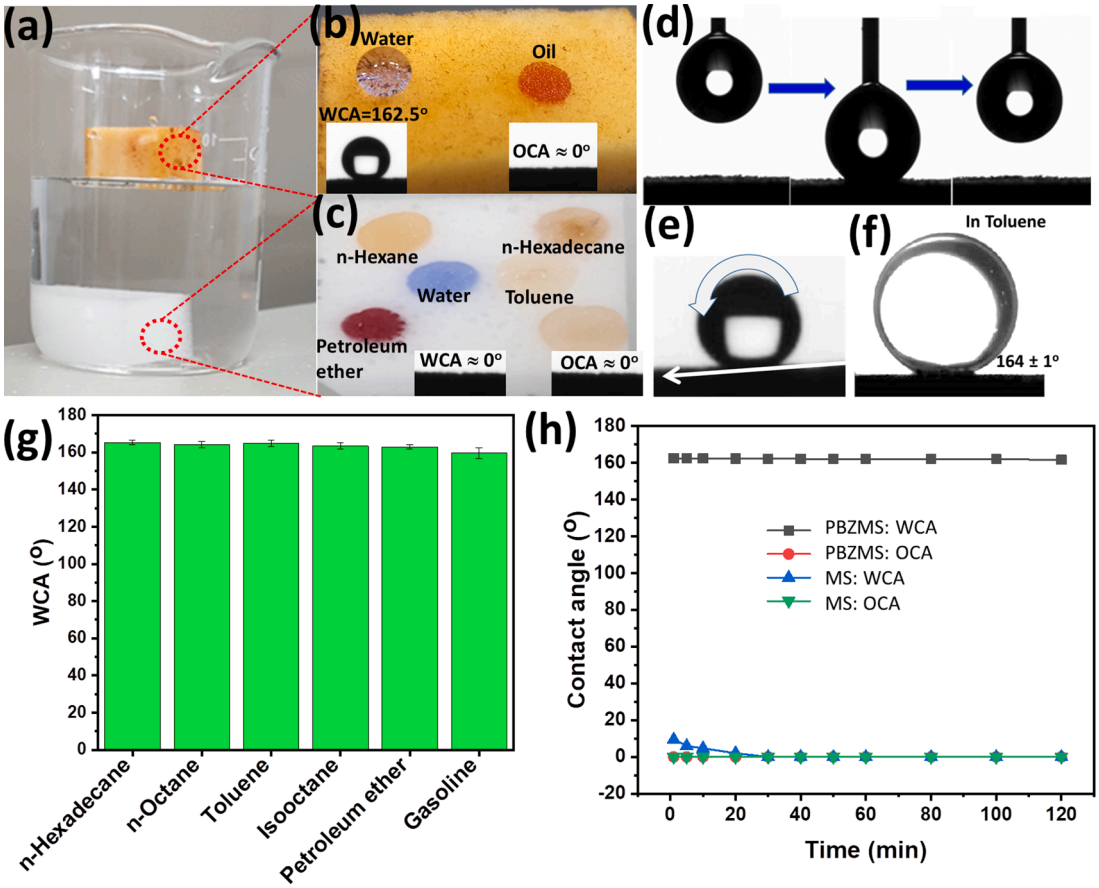

Fig. 2. Optical images of (a) MS and PBZMS in water, (b) water droplet (dyed with methylene blue) and *n*-hexadecane droplet (dyed with methyl red) on PBZMS, and (c) different oil droplets and water droplet on MS. (d) Optical photographs showing the wetting behavior of PBZMS during contact and departure of the water droplet. Optical images of (e) in air water SA and (f) underoil WCA on PBZMS. (g) WCA of PBZMS in different oils and (h) WCA and OCA of MS and PBZMS in air, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.4. Water-in-oil emulsion separation experiment

The separations of the prepared emulsions were carried out using the systematically controlled and compressed PBZMS fixed in a glass funnel with the radius of 0.552 cm employing an external pressure of 0.025 bar or only gravity-driven process. The density and the thickness of the compressed PBZMS were 0.12 ± 0.01 g cm^{-3} and 2.1 ± 0.2 cm, respectively.

2.5. Instrument characterization

The microstructures and chemical composition of MS and PBZMS were characterized using scanning electron microscopy (SEM: JEOL JSM-6500, JEOL. Ltd., Tokyo, Japan) and energy dispersive X-ray spectrometry (EDS: SEM-EDS, JSM-6500F, JOEL, Ltd., Tokyo, Japan). The contact angles of liquid droplets were measured using a Magic Droplet-100 contact angle goniometer (Sindatek instruments Co., Ltd. Taipei, Taiwan) by injecting 5 and 10 μL volumes of liquid drops for static and dynamic contact angles, respectively; each reported contact angle represents average of five measurements. Dynamic light scattering (DLS) measurements were carried out by using an SZ-100 instrument (Horiba, Ltd. Kyoto, Japan). Optical microscopy images were recorded using a KEYENCE HDR VHX-7000 instrument (Keyence Corp., Osaka, Japan) after placing a drop of the emulsion solution onto a biological counting board. Water contents in the filtrates of SWOEs were determined using a Titrator Compact C10SX (Mettler-Toledo Pac Rim AG, Greifensee, Switzerland) Coulometric Karl Fischer moisture titrator.

3. Results and discussions

Benzoxazine can undergo thermally induced ring-opening addition reactions (Fig. 1a). In a previous study, we revealed that polybenzoxazines have low surface free energies and hydrophobicities because of their strong intramolecular hydrogen bonding [20]. More recently, we reported that cured main-chain-type polybenzoxazine (P(B-pd)) films display unique flexibility, a low surface free energy (20.1 mJ m^{-2}), a high water contact angle (102°), and high glass transition temperature (T_g = 354 °C) [18]. In this study, we prepared a main-chain-type P(B-pd)-modified melamine sponge through a water-based, non-solvent-induced phase inversion method (Fig. 1b). Non-solvent-induced phase inversion and its mechanism have been studied for over 50 years, especially for the preparation of phase inversion membranes, which are extensively used in numerous environmental separation processes and chemical and biotechnology industries [21]. However, there have only been a few reports of the preparation of 3D porous materials such as sponges and foams using this method. Of these reports, almost all used organic solvents as the non-solvent component. Gao et al. reported co-solvent-incorporating innately rough, superhydrophobic coatings with self-healing properties for versatile oil–water separation using *n*-hexane as a non-solvent [22]. Zhu and coworkers successfully fabricated a fluorine-free superhydrophobic coating with a hierarchical surface structure and low surface energy via a recently developed dip-coating method combined with non-solvent induced phase separation on various substrates using *n*-hexane and ethanol as non-solvents [23]. In this study, we used water as a non-solvent; this has two advantages: the costs related to the use of organic solvents are minimized and water

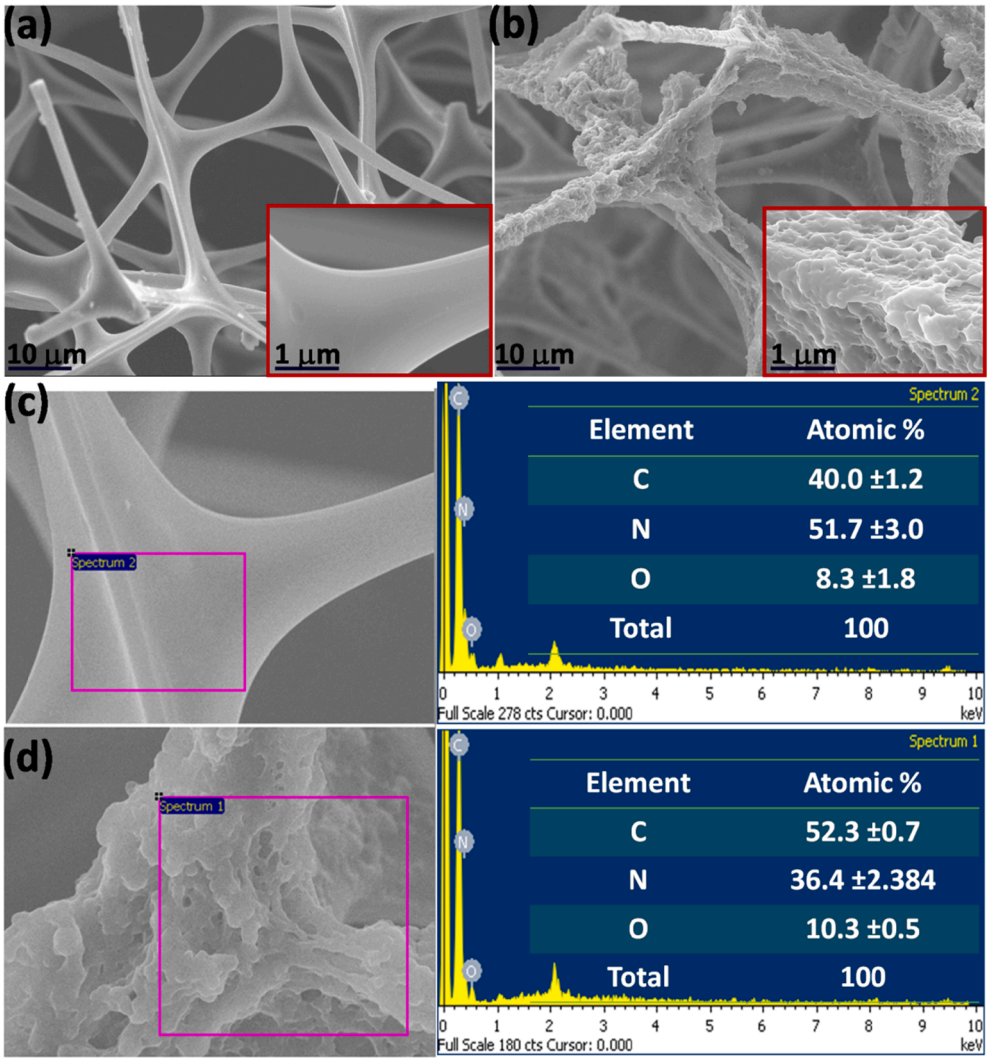

Fig. 3. SEM images of (a) MS and (b) PBZMS. SEM and EDS data of (c) MS and (d) PBZMS.

is an environmentally friendly solvent compared to the volatile organic solvents, which are toxic and cause environmental pollution [24].

In PBZMS, a coating of polymeric P(B-pd) with hydrophobic characteristics is anchored over the MS framework, thus transforming its wettability. The as-prepared PBZMS exhibited superhydrophobicity, having a water contact angle (WCA) of 162.5 ± 1.5° and superoleophilicity (oil contact angles (OCA) for isooctane, gasoline, *n*-hexadecane, toluene, *n*-hexane, petroleum ether, and *n*-octane are all close to 0°) (Fig. 2a). When water droplets were placed on the superhydrophobic surface, they retained almost round shapes and rolled off with a minimum sliding angle (SA) of 3 ± 1.4°; however, oil droplets were completely absorbed by PBZMS (Fig. 2b). On the other hand, both oil droplets and water droplets were completely absorbed by the pristine melamine sponge (MS) (Fig. 2c). In addition, the dynamic water repellence of PBZMS was investigated in air using an optical camera. To observe water droplet deformation on the surface of PBZMS, we conducted "contact and departure" experiments, as shown in Fig. 2d. Interestingly, on the surface of PBZMS, there was no obvious deformation and no residual water, revealing the extremely low water adhesion with the surface. PBZMS also displayed a high WCA in oil of 164.2 ± 1°, and no obvious deformation of the water droplet was observed during the contact tests (Fig. 2f), indicating its outstanding superhydrophobicity in oil (Fig. 2g). This is because the oil trapped in the micro-hierarchical rough surface formed on PBZMS forms a stable water-repelling skeleton to reduce the opportunity for contact between water and PBZMS. In addition, the resistance of the superoleophilicity and superhydrophobicity of PBZMS were evaluated by monitoring the dynamic WCA and OCA of PBZMS over 2 h, and they were found to be almost constant without any significant changes (pristine MS was used for comparison) (Fig. 2h).

The effect of P(B-pd) concentration in the polymer solution on the wettability of the PBZMS surface was studied by conducting WCA and SA measurements. The WCA of PBZMS increased from 120° to 162° as the concentration of P(B-pd) was increased from 0.5 to 30 mg mL^{-1}, and the SA decreased from 15° to 3°(Fig.S1) over the same period. Further increase in the concentration of P(B-pd) had no significant effect on the superhydrophobicity of PBZMS. Hence, 30 mg mL^{-1} was chosen as the optimal concentration for further studies.

The morphologies of MS and PBZMS were investigated using scanning electron microscopy (SEM) (Fig. 3a and b). As shown in Fig. 3a, the surface morphology of MS was relatively smooth. Fig. 3b, which is at higher magnification, shows that the framework of PBZMS is covered by numerous nano-/microscale protrusions consisting of hydrophobic P(B-pd). Compared with that of MS, the surface of PBZMS was much rougher, and this is a reason for the superhydrophobicity. Next, we used X-ray energy dispersive spectroscopy (EDS) to determine the chemical compositions of MS and PBZMS (Fig. 3c and d). The coverage of the MS surface by P(B-pd) was confirmed by the decrease in the nitrogen content compared to that of bare MS [4].

Generally, harsh environmental conditions, for example, corrosive

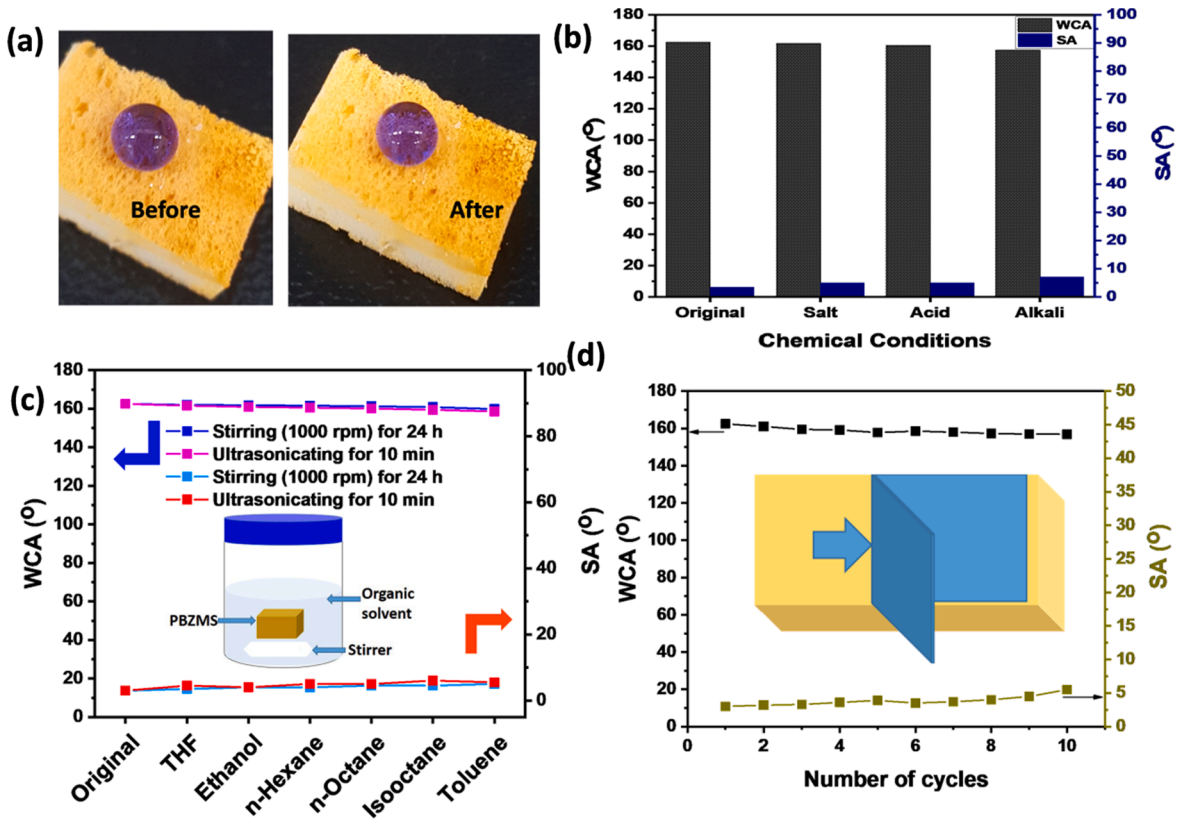

Fig. 4. (a) Digital images of water droplets on PBZMS before and after immersion in HCl. Plots of WCA and SA as a function of (b) different chemical conditions after the immersion of PBZMS in aqueous HCl (pH = 1), NaOH (pH = 12), and NaCl (3.5 wt%) for 72 h, (c) effect of organic solvents on the wettability of PBZMS after stirring at 1000 rpm for 24 h and with ultrasonication for 10 min (*inset*: digital images of continuous stirring treatment system), and (d) the number tape test cycles for PBZMS.

aqueous solutions, affect the hydrophobicity of superhydrophobic materials significantly. In a previous report, Wang et al. revealed that superhydrophobic polybenzoxazine surfaces possess superhydrophobicity towards both pure water and alkaline and acidic water [25]. In this study, P(B-pd) showed excellent stability in acidic (pH = 1), alkaline (pH = 12), and saline (3.5 wt% NaCl) aqueous solutions during 72-h immersion tests (Fig. 4). As shown in Fig. 4a, the appearance of water droplets on the surface before and after immersion in HCl (pH = 1) for 72 h is almost the same. As shown in Fig. 4b, the immersion tests did not result in significant changes in the WCA and SA of PBZMS. Moreover, the solvent resistance of PBZMS was examined through continuous and vigorous stirring treatments with different organic solvents. After vigorous stirring at 1000 rpm for 24 h using ethanol, tetrahydrofuran (THF), *n*-octane, toluene, *n*-hexane, and isooctane, the WCA of PBZMS was still greater than 150° (Fig. 4c). Further, PBZMS retained its superhydrophobic property even after ultrasonic treatment for 10 min in these organic solvents, confirming the high stability and solvent-resistance of PBZMS. On the other hand, the poor adhesion strength of the fabricated superhydrophobic coatings is a serious problem limiting its use in industrial applications [26]. A test with Scotch Tape was used to evaluate the adhesion strength of the P(B-pd) coating on MS. In this test, the tape was pressed against the coating and then peeled off; this was repeated 10 times. Fig. 4d shows that PBZMS retained its superhydrophobicity (the WCA and SA are 157° and 5.5°, respectively) after performing 10 adhesion tests, thus confirming the excellent stability of PBZMS.

For practical application, the absorption capacity and reusability are two key factors for oil-absorbing materials. Thus, a gravimetric method was employed to measure the absorption capacities of PBZMS, and the gravimetric absorption capacities ($Q_{m/m}$) of PBZMS for organic solvents/oils were evaluated using equation (1).

$$Q_{m/m} = \frac{(m_a - m_d)}{m_d} \quad (1)$$

Here, m_d is the mass of the dry PBZMS, and m_a is the mass of PBZMS after absorption.

As shown in Fig. 5a and b, PBZMS can selectively absorb oil from water both in air and water once it has made contact with the oil–water mixtures because of its superoleophilic and superhydrophobic properties. Thus, PBZMS is an excellent absorbent material for the selective removal of oils/organic pollutants from water. Further, PBZMS exhibited outstanding gravimetric absorption capacities for oils/organic liquids ranging from 62 g/g (for *n*-hexane) to 170 g/g (for chloroform) (Fig. 5c) owing to the 3D structure of MS with a large inner volume and high porosity (>99%) [27]. Compared to various other types of superhydrophobic MS-based materials, PBZMS has higher absorption capacities than many of them for both dichloromethane (Fig. 5d) and chloroform (Fig. S2) solvents used for comparison [16,28–41]. The gravimetric absorption capacity of PBZMS is greater than that of polybenzoxazine-modified superhydrophobic porous materials in the previous works (Table 1) [4,30,38–40]. The superior oil adsorption performance of PBZMS to most MS-based superhydrophobic materials may be attributed to the comparatively low blockage of some small pores in PBZMS after modification. However, this adverse structure could be observed in other MS-based superwetting materials in which it could reduce the efficient absorption space. To estimate the recyclability potential of PBZMS, a simple manual immersion–squeezing test was used. As shown in Fig. 5e, PBZMS maintained more than 80% of its initial absorption capacity and its WCA of 150.5°, even after 50 continual absorption–desorption processes, indicating good reusability.

Wastewater containing complex emulsified water/oil mixtures is a serious concern and is produced by various industrial processes.

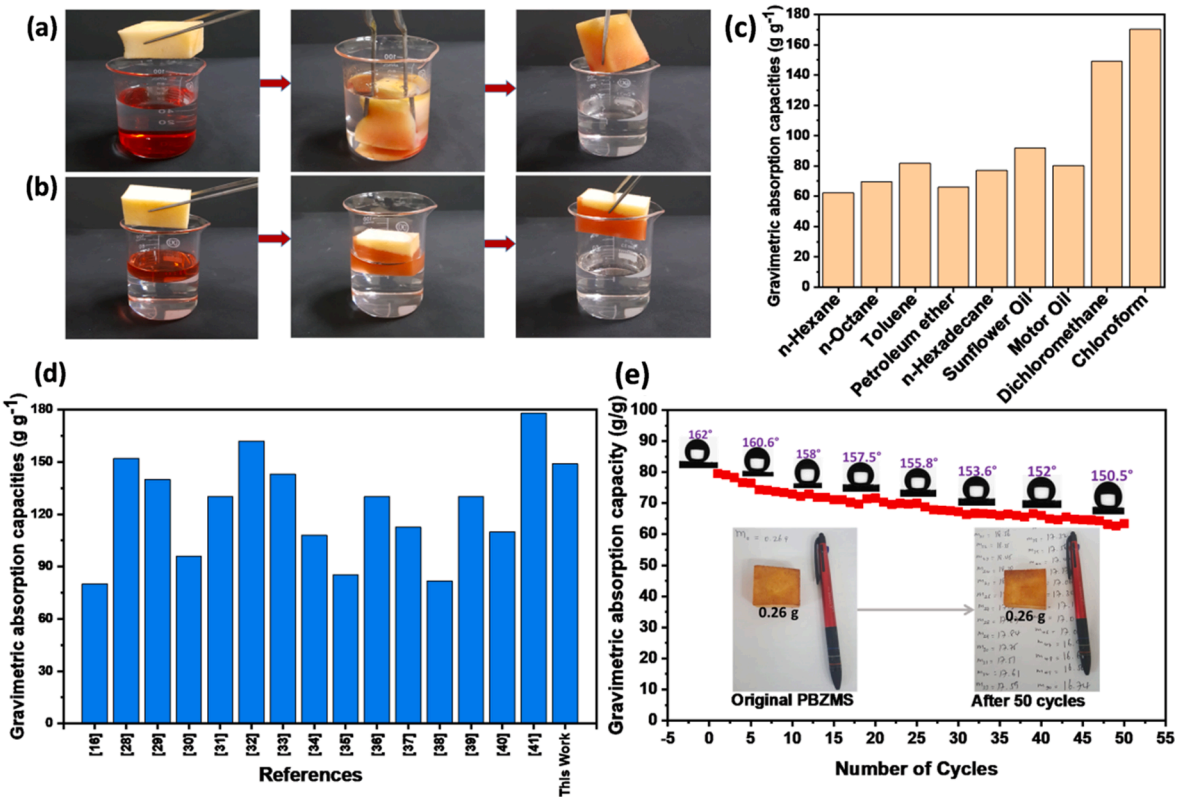

Fig. 5. Images of the removal processes of (a) dichloromethane (dyed with oil red) by PBZMS submerged in water and (b) *n*-hexane floating on water. (c) Gravimetric absorption capacities of PBZMS for different oils and organic solvents. (d) Gravimetric absorption capacities of PBZMS (this work) compared with those of other super-/hydrophobic MS-based composites using dichloromethane. (e) Gravimetric absorption capacity of PBZMS using toluene with a cyclic squeezing process. Insets are the WCAs through the cycling tests measured at seven-cycle intervals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Gravimetric absorption capacities comparison of PBZMS with other super-hydrophobic polybenzoxazine-modified MS for dichloromethane and chloroform solvents.

S. N.	Coated material	WCA (°)	Dichloromethane/ chloroform	Gravimetric absorption capacity (g/g)	Ref.
1	CR-PBz-sponge	>150	Chloroform	120	4
2	FPBZ/ SiO_2@MS	>150	Dichloromethane	96	30
3	PBZ-SiO_2@MS	>150	Dichloromethane Chloroform	82 94.7	38
4	PB-MS(*x*)	140	Dichloromethane Chloroform	129 140.12	39
5	PBz/r-GO@CS	>150	Dichloromethane Chloroform	110 123	40
6	PBZMS	162	Dichloromethane Chloroform	149 170	This work

Surfactant-stabilized emulsions are challenging to treat compared to simple oil–water mixtures, so new advanced materials for the efficient separation of these emulsions are in demand. Recently, porous-structured 2D and 3D superwetting materials have attracted considerable attention for emulsion separation in industrial oily wastewater treatment [1]. Herein, based on the results obtained with 3D MS, as well as its flexibility and squeezability, we developed a compression technique to decrease the pore diameter of the sponge framework to generate small channels for the separation of various water-in-oil emulsions. Although PBZMS can remove bulk oil from water, the uncompressed structure should be incapable of separating water-in-oil emulsions because of the large pore size of the sponge (≥50 μm), which is much larger than the water droplets in the emulsions. Remarkably, we found that PBZMS effectively separates various SWOEs by both gravity-driven and pressure-driven (0.025 bar) processes. Fig. 6a and b show the optical microscopy images of the original and compressed PBZMS, respectively. Compared with that of the original sample, the surface morphology of the compressed sample is changed, and the PBZMS framework is more compact. Fig. 6c shows a schematic of the setup used for SWOE separation via gravity-driven separation through compressed PBZMS. The emulsions and filtrates obtained by gravity-driven and pressure-driven processes were observed by optical microscopy (Fig. 6d and e, respectively). Numerous microscopic water droplets are present in the opaque water-in-toluene emulsion, whereas the droplets are not presentin the transparent oil phase after separation. Further, both gravity-driven and pressure-driven processes yielded similar separation performance.

The particle size distributions of the water-in-toluene emulsions obtained using both separation processes before and after separation were measured using dynamic light scattering (DLS) (Fig. S3). The droplet size changed from 2480 ± 410 nm (Fig. S3a) to 58.8 ± 4.9 nm (Fig.S3b) for the gravity-driven separation process and to 99.7 ± 9.4 nm (Fig.S3c) for the pressure-driven process (0.025 bar).These results indicate that the compressed PBZMS shows excellent performance in the separation of different SWOEs.

In the separation, of SWOEs including *n*-hexane, petroleum ether, gasoline, *n*-octane, isooctane, toluene, and *n*-hexadecane, the fluxes were astonishingly high: 13,900 ± 300, 13,400 ± 250, 12,900 ± 380, 12,500 ± 300, 12,130 ± 340, 11,100 ± 200, and 2120 ± 50 L m^{-2} h^{-1}, respectively, under gravity alone (Fig. 7a). Similarly, the fluxes of these SWOEs emulsions upon the application of 0.025 bar applied pressure

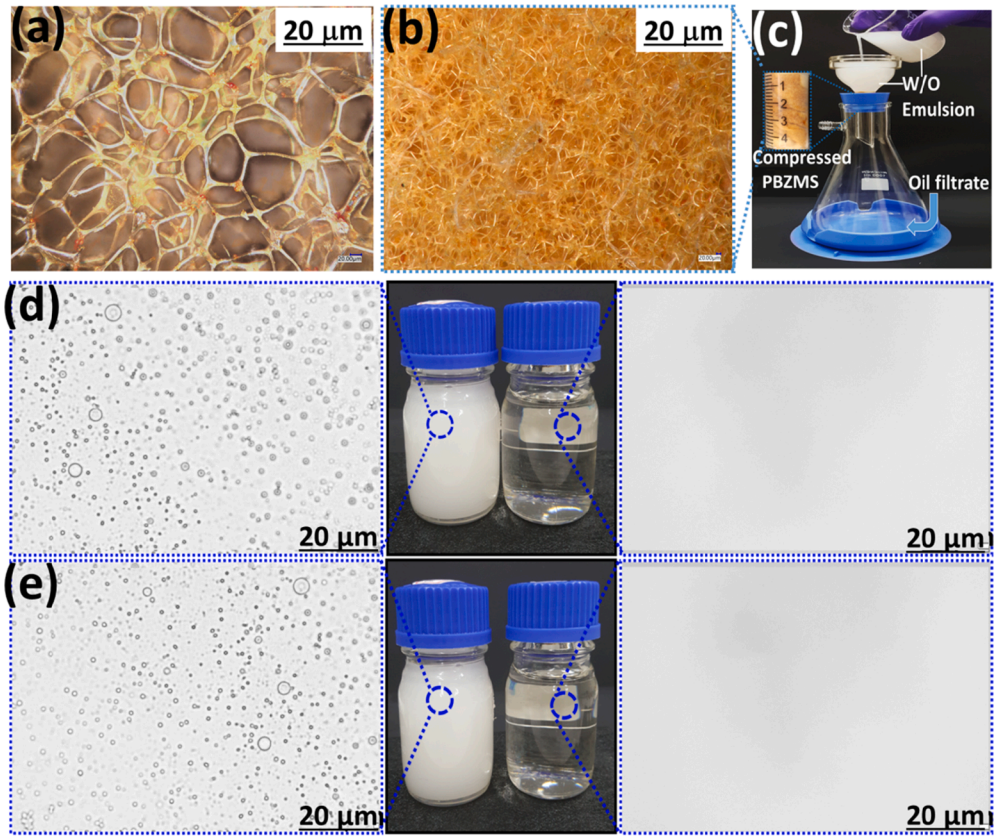

Fig. 6. Optical microscopy images of the (a) uncompressed and (b) compressed PBZMS. (c) Schematic of our filtration system using compressed PBZMS for SWOE separation. (d, e) Optical microscopy pictures of water-in-toluene emulsions and the corresponding filtrates (left and right, respectively) obtained by (d) gravity-driven and (e) pressure-driven processes.

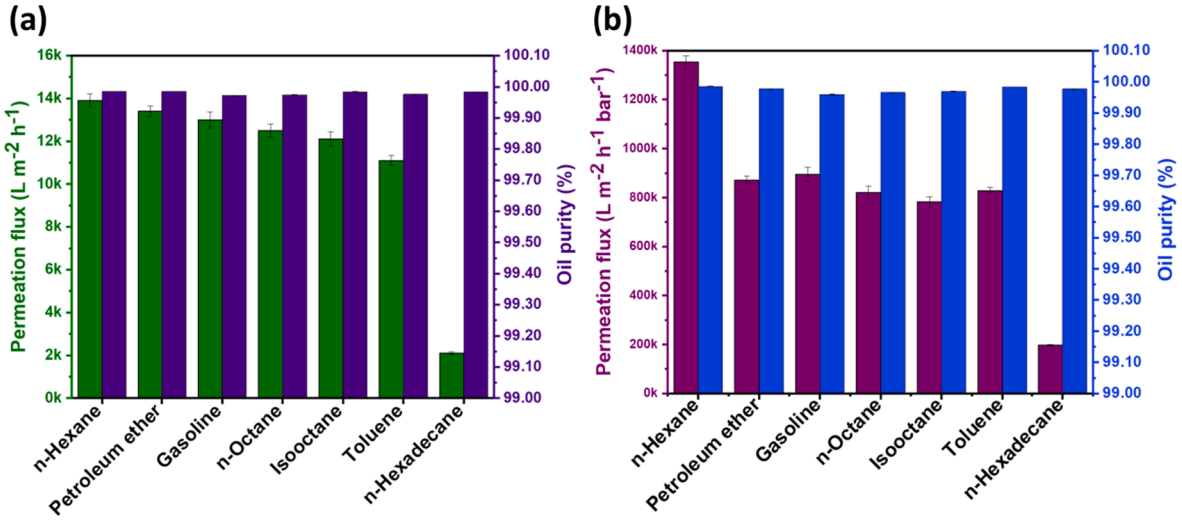

Fig. 7. Separation performance of PBZMS on SWOEs obtained via (a) gravity-driven and (b) pressure-driven processes.

were 1,353,000 ± 27,700, 895,100 ± 28,800, 872,100 ± 16,600, 828,600 ± 11,900, 820,200 ± 21,200, 781,900 ± 26,100, and 197,800 ± 2500 L m^{-2} h^{-1} bar^{-1} for *n*-hexane, gasoline, petroleum ether, toluene, *n*-octane, isooctane, and *n*-hexadecane, respectively (Fig. 7b). Generally, excellent separation performance was achieved under both separation conditions, confirming that the separation performance of PBZMS does not decline on the application of pressure. As shown in Fig. 7, the oil purities of all separated emulsions were ≥99.96 wt%, and a few reached 99.99 wt%, demonstrating very high separation efficiencies.

A few studies have been reported on separating SWOEs using 3D porous materials via compression [42]. Yang et al. developed a novel compression strategy for a 3D superhydrophobic sponge for the effective separation of water-in-oil emulsions [43]. Kaang and coworkers prepared a compressed superhydrophobic melamine sponge with excellent performance for the separation of a water-in-oil emulsion [44]. Very recently, our research group prepared superhydrophobic/superoleophilic cotton-based materials for the separation of SWOEs at

Table 2
Comparison of the SWOE separation performance of PBZMS with those of various superwetting polybenzoxazine-modified materials.

S. N.	Material	Gravity-driven		Pressure-driven		Reference
		Flux (L m^{-2} h^{-1})	Oil purity (wt.%)	Flux (L m^{-2} h^{-1} bar^{-1})	Oil purity (wt.%)	
1	FPBZ/ SiO2@MS	1500	97.6	–	–	3
2	CR-PBZ@CM	430	99.94	–	–	4
3	PBZ-SiO2-MS	1300	99.78	–	–	38
4	Metal-coordinated PBZ	2100	>99	37,526	>99	45
5	F-PBZ/Al_2O_3 NPs	892	–	–	–	46
6	PBZMS	13,923	99.96	1,353,000	99.96	This Work

*Not Reported.

extremely high fluxes and with excellent efficiencies using a compression strategy [19]. However, the separation performance of PBZMS is better than those reported in previous studies. Moreover, as shown by the data in Table 2, the SWOE separation performance of PBZMS is far greater than that of any polybenzoxazine-based-modified materials [3,4,38,45,46]. Other superwetting materials have been shown to separate water-in-oil emulsions with high fluxes (Table 3) and were selected for comparison [11,12,19,42,43,47–52]. Compared to these superwetting materials, PBZMS exhibited extremely high fluxes with outstanding efficiencies for the separation of SWOEs.

Antifouling properties and recyclability are important for the filtration of materials during oil–water separation processes. The antifouling property of PBZMS was evaluated by performing cyclic separation experiments using surfactant-stabilized water-in-petroleum ether emulsions. In these experiments, the separation was driven by the application of pressure. For each of the five cycles, 100 mL of the emulsion was passed through the compressed PBZMS. As shown in Fig. 8, a slight decrease in flux was observed in each cycle. After washing with acetone, the flux recovered completely and was even higher than the original flux in all cycles. The minimum oil purity was 99.92 wt% after 5 cycles, revealing the remarkable separation performance. The results confirm

Table 3
SWOE separation performance: Comparison of PBZMS with different superwetting materials.

S. N.	Material	Gravity-driven		Pressure-driven			Reference
		Flux (L m^{-2} h^{-1})	Oil purity (wt. %)	Flux (L m^{-2} h^{-1} bar^{-1})	Oil purity (wt. %)	External pressure applied (bar)	
1	Superhydrophobic copper foam	6560	99.89	–	–	–	11
2	Silicone-nanofilament-coated porous glass substrates	6200	99.99	120,000	99.98	–	12
3	Superhydrophobic cotton-based material	10,400	99.98	867,516	99.97	0.1	19
4	Hydrophobic-polymer-coated melamine sponge	–	–	155,000	99.98	0.1	42
5	superhydrophobic 3D melamine sponge	–	–	32,500	99.96	–	43
6	SWCNT-based bilayer membrane	–	–	48,300	99.95	0.01	47
7	Acrylonitrile–butadiene-styrene copolymer coated on filter paper	–	–	13,000	99.90	0.9	48
8	SiO_2-NP-treated PVDF membrane	–	–	16,400	99.95	0.9	49
9	PFDTS/CNT hybrid membrane	–	–	41,880	99.89	0.9	50
10	SWCNT network films	–	–	16,810	99.95	0.1	51
11	Cellulose Aerogel/membrane composite	12,890	99.5	–	–		52
12	PBZMS	13,923	99.96	1,353,000	99.96	0.025	This Work

*Not Reported.

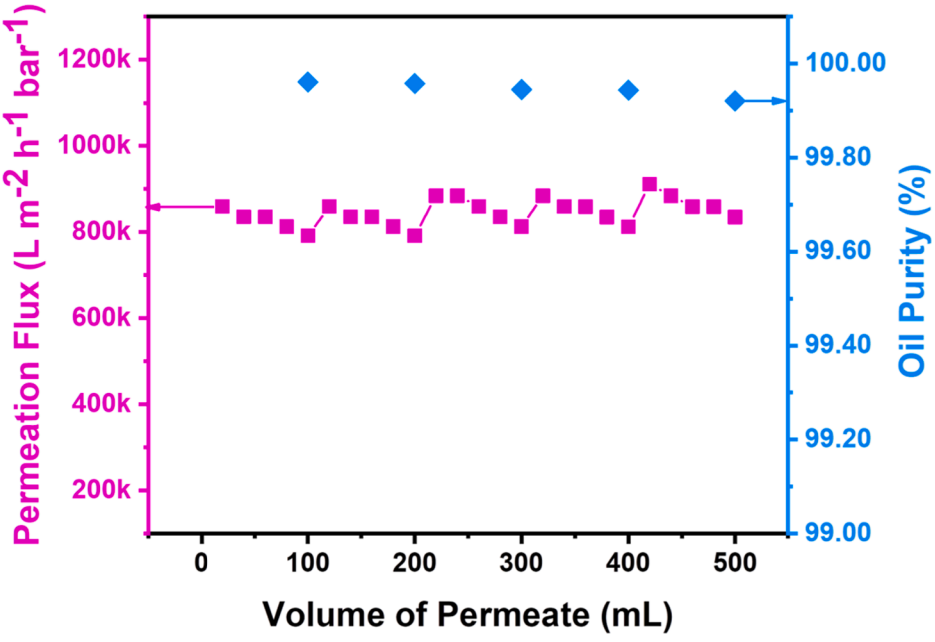

Fig. 8. Real-time monitoring of the separation flux and oil purity during cyclic separation tests using PBZMS for the separation of surfactant-stabilized water-in-petroleum ether emulsion.

the promising antifouling properties and recyclability of PBZMS for the treatment of water-in-oil emulsions.

The antifouling properties of PBZMS were also evaluated using water dyed with methyl blue and compared with those of MS (Fig.S4a and S4b). As shown in the figures, PBZMS was not dyed after immersion because of its antifouling properties, whereas MS was easily dyed with the methyl blue mixture.

4. Conclusions

In this study, we prepared PBZMS from main-chain-type polybenzoxazine (P(B-pd)) and melamine sponge through a facile water-based non-solvent-induced phase inversion method. PBZMS possessed superhydrophobicity, having a WCA of 163°, and superoleophilicity, having an OCA of approximately0°. PBZMS exhibited promising separation performance in different oil/water mixtures. The prepared superwetting material has high absorption capacities for different oils (up to 170 times their weight), and the compressed PBZMS exhibited outstanding separation performance of various SWOEs, exhibiting very high permeation fluxes of up to 13,900 L $m^{-2}h^{-1}$ and 1,353,000 $m^{-2}h^{-1}$ bar^{-1} through both gravity-driven and pressure-driven processes, respectively, with excellent efficiency (an oil purity of $\geq$ 99.96 wt%). The outstanding separation performance for various organic solvents and oils, stability in harsh physical and chemical environments, antifouling properties, and recyclability of PBZMS make it an excellent candidate for large-scale applications.

CRediT authorship contribution statement

Dula Daksa Ejeta: Conceptualization, Methodology, Investigation, Writing - original draft. **Chih-Feng Wang:** Resources, Supervision, Conceptualization, Writing - review & editing. **Ching-Hsuan Lin:** Resources, Supervision, Conceptualization, Writing - review & editing. **Shiao-Wei Kuo:** Resources, Formal analysis. **Jem-Kun Chen:** Resources, Formal analysis. **Hsieh-Chih Tsai:** Resources, Formal analysis. **Wei-Song Hung:** Resources, Formal analysis. **Chien-Chieh Hu:** Resources, Formal analysis. **Juin-Yih Lai:** Resources, Funding acquisition, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2021.118387.

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