REVIEW ARTICLE

Bionic functional membranes for separation of oil-in-water emulsions

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Abstract: The separation of oil-in-water emulsion is an urgent challenge because its massive production and discharge from daily and industrial activities have caused severe hazards to the ecosystem and serious threats to human health. Membrane technology is considered an outstanding solution strategy for the separation of oil-in-water emulsions due to its unique advantages of low cost, high efficiency, easy operation, and environmental friendliness. However, the membrane is easily fouled by the emulsion oil droplets during the separation process, causing a sharp decline in permeation flux, which greatly inhibits the long-term use of the membrane and largely shortens the membrane's life. Recently, it was found that endowing the membranes with special wettability e.g., superhydrophilic and superoleophobic can greatly enhance the permeability of the continuous water phase and inhibit the adhesion of oil droplets, thus promoting the separation performance and anti-oil-fouling property of membrane for oily emulsions. In this paper, we review and discuss the recent developments in membranes with special wettability for separating oil-in-water emulsions, including the mechanism analysis of emulsion separation membrane, membrane fouling issues, design strategies, and representative studies for enhancing the membrane's anti-oil-fouling ability and emulsion separation performance.

Keywords: bionic surface; membranes; wettability; oil-in-water emulsions; oil–water separation

1 Introduction

Oily wastewater is widely produced in our industrial production and daily life, such as oil extraction, mechanical manufacturing, food processing, energy, and chemical industries [1–3]. According to incomplete statistics, about 2 million tons of oily wastewater are discharged into the water every day worldwide [4]. China's oil extraction industry alone has about 500 million tons of oilfield-produced water that needs to be treated every year. The discharge of untreated oil-water mixtures into nature can cause serious water pollution, environmental damage, and health threats [5–7]. Oily wastewater can be divided into free oil-water mixtures and emulsion oil-water mixtures

according to the particle size of the dispersed phase (oil droplets) [8–10]. The particle size of the dispersed phase in the free oil-water mixture is large, and after a long period of standing, the oil-water will be quickly stratified due to the density difference, which can be easily separated. However, the size of the emulsion oil droplets usually ranges from several hundred nanometers to tens of microns when dispersed in oily wastewater (oil in water emulsion). In addition, due to various surfactants adsorbed on the interface of the emulsion oil droplets to form a stable interface film, which makes the emulsion oil droplets even in a collision is not easy to gather and fuse, increasing the separation difficulty of the emulsion oil and water [11–15]. Therefore, how to achieve

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efficient separation and recovery of oily emulsions has become a global challenge and has attracted the widespread attention of scientists and engineers all over the world. As shown in Fig. 1, the research on oil-water separation has grown explosively over the past two decades.

The traditional technologies for the separation of oil-water mixtures mainly include the gravity method [16], centrifugal method [17], air flotation method [18], high-pressure electrostatic method [19], chemical demulsification method [20], biodegradation method [21], and membrane separation method [22]. Among them, the membrane separation method has drawn widespread attention in the field of oil-water separation because of its advantages of low cost, low energy consumption, simple operation, and no secondary pollution [4, 23–26]. The main working mechanism of the membrane separation method is the "size screening" effect, which can intercept the emulsion oil droplets larger than their pores and achieve the separation of the oil-in-water emulsion. However, trapped emulsion oil droplets on the membrane will cause membrane contamination, thus resulting in reduced separation performance. With the deepening of the study of surface wettability, the oil-water separation efficiency and the anti-pollution ability of the filter membrane have been improved greatly by adjusting the wettability of the membrane for oil phase and water phase, based on the difference in oil-water surface tension [27–29]. For example,
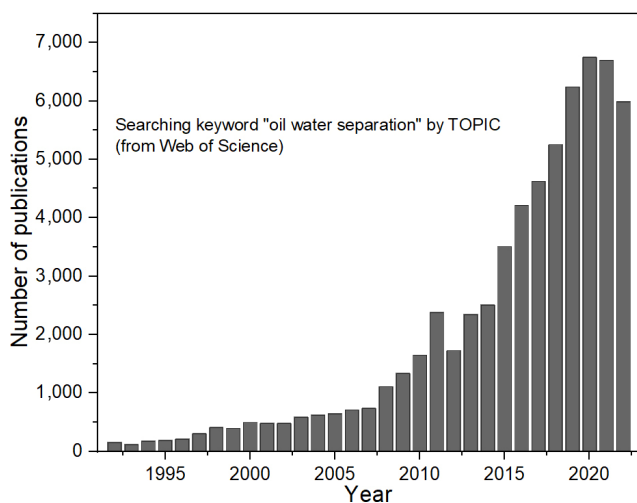
superhydrophilic-superoleophobic filter membranes [30–32] can promote the permeation efficiency of the water phase and enhance the oil resistance of the membrane. However, to ensure the effective separation of oil and water, the pores of the superwetting membrane need to be smaller than the diameter of the emulsion oil droplets to be treated. At the same time, the trapped emulsion oil droplets will continue to accumulate on the surface and pores of the filter membrane, which causing serious membrane blockage and membrane fouling, eventually resulting in a reduced oil-water separation performance or even failure. To address the membrane fouling issue and improve the separation performance of membranes, researchers have made lots efforts on developing new membrane materials and membrane technologies.

To this end, we summarized the recent developments in the separation of oil-in-water emulsions by using membranes with special wettability. First, the working mechanism and current challenges of membranes for separating oil-in-water emulsions are analyzed and discussed in detail. Second, the recent progress of membranes with special wettability for oily emulsion separation is reviewed. The types of materials and fabrication process of the oil-water separation membranes are summarized, and their oil/water separation performance is discussed. Finally, the future outlook of membranes with special wettability for the separation of oily emulsion is discussed.

2   Mechanism of membranes for separation of the oil-in-water emulsion

According to the difference in working mechanism, the membranes for separating oil-in-water emulsion can be divided into two categories: (1) size-sieving membrane (Fig. 2(a)) and (2) demulsification membrane (Fig. 2(b)). For the size-sieving membrane, when the oil-in-water emulsion is in contact with the membrane, the water phase is allowed to permeate through the membrane freely, whereas the emulsion oil droplets are intercepted by the membrane surface. For the demulsification membrane, when the oil-in-water emulsion permeates through the membrane, the emulsion oil droplets are captured by the membrane
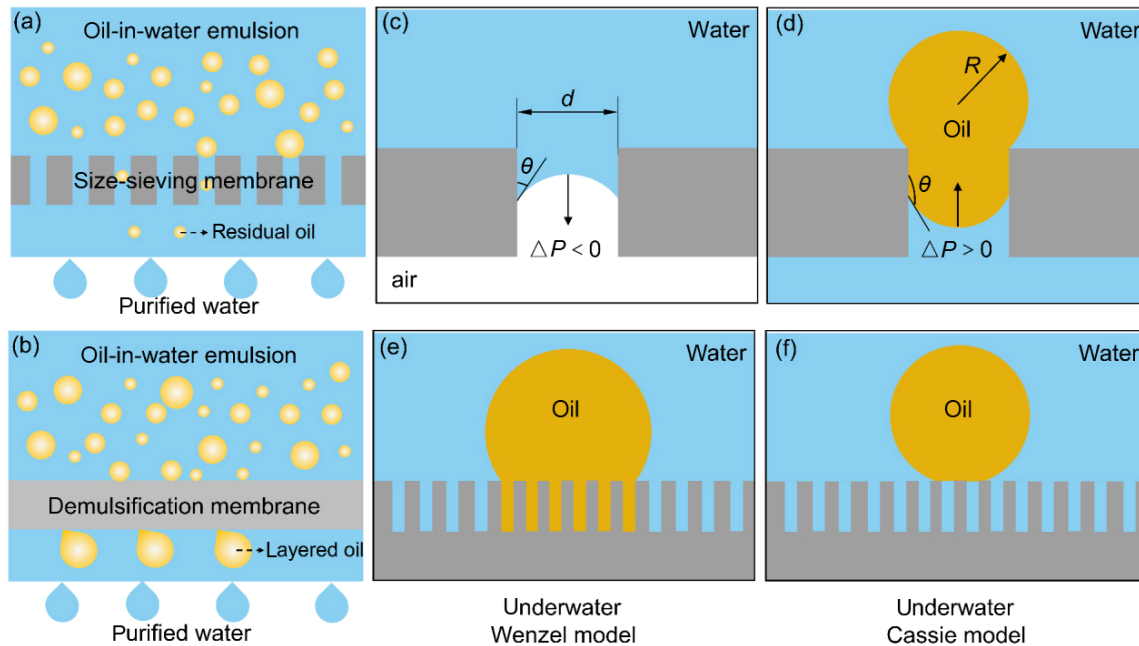

Fig. 1 Number of publications on the topic of oil–water separation (indexed in ISI Web of Science).

Fig. 2 (a) Membranes for separating oil-in-water emulsion based on size-sieving mechanism; (b) membranes for separating oil-in-water emulsion based on demulsification mechanism; (c) schematic of the water wetting on the membrane pore; and (d) schematic of an oil droplet at a pore entrance of membrane. Schematic of the wetting states of an oil droplet on the membrane in the water environment: (e) underwater Wenzel state and (f) underwater Cassie state.

media and gradually coalesce into enlarged oil droplets (hundreds of microns). Subsequently, the oil droplets detach from the surface of the membrane and form an unstable oil-water mixture in which the oil phase and water phase can be automatically separated by gravity. The quick permeation of the water phase and the efficient interception or capture of emulsion oil droplets are the two main tasks for the membranes for the separation of an oil-in-water emulsion.

The wetting models of the water phase and emulsion oil droplet on a membrane pore are shown in Figs. 2(c) and 2(d). The pressure at which a liquid can enter a membrane pore is known as breakthrough pressure (ΔP_{crit}). The Young–Laplace equation was generally used to estimate the value of breakthrough pressure [33–35]:

$$\Delta P_{crit} = -\frac{2\gamma_L \cos\theta}{d/2} \tag{1}$$

where γ_L represents the liquid surface tension and θ represents the static contact angle of the liquid on a smooth membrane surface. The d represents the diameter of the membrane pore. It can be deduced

from the above equation that the value of breakthrough pressure was determined by the contact angle, liquid surface tension, and membrane pore size, which can be positive or negative. Therefore, the following conclusions can be drawn. First, a negative value of breakthrough pressure can be obtained when the contact angle is less than 90°. In this situation, the liquid can automatically enter the membrane pore without resorting to any external pressure. Second, if the contact angle is higher than 90°, the value of breakthrough pressure would be positive, which means the membrane can block the liquid with external pressure less than the critical value from entering membrane pores. Besides, increasing the contact angle and decreasing membrane pores can be used to create a high breakthrough pressure. Therefore, increasing the hydrophilic property and pore of the membrane is beneficial for enhancing the water permeability of the membrane (Fig. 2(c)).

The model of an emulsion oil droplet intercepted by a membrane pore is shown in Fig. 2(d), in which the membrane pore with a size smaller than the oil droplet [36–38]. Different from the interception of

solid particles, the oil droplets can be squeezed into the membrane pore because they are deformable. The critical pressure (ΔP_{cri}) required for an oil droplet to enter the membrane pore can be calculated by Eq. (2) [39, 40]:

$$\Delta P_{cri} = -2\gamma_{OW}\frac{\cos\theta}{r_{pore}}\cdot$$

$$\left\{1-\left[\frac{2+3\cos\theta-(\cos\theta)^3}{4(\frac{r_{drop}}{r_{pore}})^3(\cos\theta)^3-(2-3\sin\theta+(\sin\theta)^3)}\right]^{1/3}\right\} \quad (2)$$

where γ_{OW} represents the interfacial tension of the oil/water interface. θ is the underwater contact angle of the oil droplet. r_{pore} is the radius of the membrane pore. r_{drop} is the radius of the oil droplet. It can be seen that the critical pressure of oil droplets depends on not only the underwater contact angle and membrane pore but also the oil droplet's size. Larger oil droplets possess larger critical pressure. In the limit $r_{drop}\rightarrow\infty$, Eq. (2) converges to Eq. (1), which represents the situation of a continuous oil film on the membrane. Besides, to prevent the oil droplet from entering the membrane pore, the membrane should be oleophobic ($\theta > 90°$). The wetting states of an underwater oil droplet on the membrane can be described by the underwater Wenzel model (Fig. 2(e)) and underwater Cassie model (Fig. 2(f)) [41–43]. The underwater contact angle of an emulsion oil droplet on the membrane is increased with the decrease of contact area between the solid surface and the oil droplet. Hence, adjusting the micro/nano-structure of membranes is an efficient approach to increase the underwater contact angle of the emulsion oil droplets on the membrane. Therefore, from the aspect of promoting the interception efficiency of the membrane and inhibiting the emulsion oil droplets from entering the membrane pores, the underwater contact angle of oil droplets on the "size-sieving" membrane should be as large as possible and the membrane pore should be as small as possible.

The theoretical permeation flux of water through the membrane can be predicated by using the Hagen–Poiseuille equation [44, 45]:

$$J = \varepsilon r_p^{\ 2}\Delta P / (8\mu L_m) \quad (3)$$

where J represents the theoretical permeation flux of the membrane. ε and r_p is the porosity and equivalent radius of the membrane, respectively. L_m represents the membrane thickness. ΔP represents the pressure difference across the membrane (driving pressure). μ is the dynamic fluid viscosity of water. It can be seen from Eq. (3) that the permeation flux of water through the membrane is proportional to the square of the membrane pore radius, the membrane porosity, and the driving pressure. Meanwhile, it is inversely proportional to the membrane thickness.

Based on the above discussions, the design of a "size-sieving membrane" for separation of oil-in-water emulsion needs to consider the following points: (1) suitable membrane pore and driving pressure to balance the interception of emulsion oil droplet and the permeation of water; (2) membrane wettability should be as hydrophilic and oleophobic as possible; (3) the membrane porosity should be as high as possible; and (4) the membrane should be as thin as possible.

3 Current challenges for membrane separation for oil-in-water emulsion

Figure 3(a) illustrates the typical permeate flux variation of filtrate through a membrane when the feed solution is pure water (region I), oil-in-water emulsion (region II), and again pure water (region III) in order [46–49]. In region I, the permeate flux keeps at a high and stable state, which is because the pure water would not pollute the membrane. In region II, as the membrane is gradually polluted by the emulsion oil droplets, the membrane pores are blocked, which leads to a gradual decrease in permeation flux over time. In the region III, the permeate flux is partially recovered by washing the membrane with pure water, which is because partially emulsion oil droplets are removed from the membrane pore. At present, how to promote the anti-fouling ability of the membrane and slow down the decline of permeate flux of the membrane has become a huge challenge.

Four types of oil fouling models are illustrated in Figs. 3(b)–3(e) [46]. At the early filtration stage, the
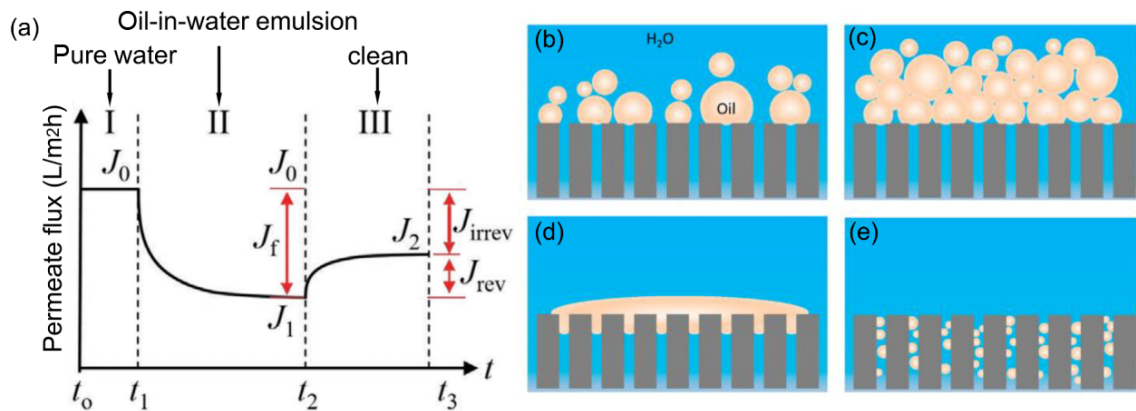
Fig. 3 (e) Schematic illustration of typical permeate flux of filtrate through the membrane when the feed solution is pure water (region Ⅰ); oil-in-water emulsion (region Ⅱ); and again pure water (region Ⅲ). (b–e) Schematic illustration of typical membrane fouling model by the emulsion oil droplets during the separation process of oil-in-water emulsion: (b) partial surface membrane pores are blocked by emulsion oil droplets; (c) emulsion oil droplets cake layer is formed on the membrane surface; (d) the contiguous oil film is formed on the membrane; and (e) emulsion oil droplets block within the membrane pores [46]. Reproduced with permission from Ref. [46], © Elsevier B.V., 2018.

intercepted emulsion oil droplets by the membrane surface will block partially membrane pores (Fig. 3(b)). With the increase of the filtration time, the emulsion oil droplets continue to accumulate on the surface of the membrane to form a filter cake, causing most of the membrane pores to become clogged (Fig. 3(c)). The oil droplets on the membrane surface are thermodynamically unstable and may merge with the adjacent oil droplets under the action of contact and extrusion to form a larger oil droplet, which can be easily removed from the oleophobic membrane surface. As shown in Fig. 3(d), when the external pressure exerted on the emulsion oil droplet is greater than its critical pressure, the oil droplets will be partially squeezed into the membrane pores, which may agglomerate laterally on/within the film to form a contiguous oil film. The formed oil film will result in serious membrane fouling problems because it cannot be removed easily. Besides, the oil film is more easily formed on the oleophilic membrane surface. As illustrated in Fig. 3(e), if the size of emulsion oil droplets is smaller than that of the membrane pores or the external pressure exceeds the critical pressure of the membrane, the emulsion oil droplet would spontaneously enter or be squeezed into the membrane pores. The trapped oil droplets are not easy to be cleaned, which causes internal fouling within the membrane pores [50].

4 Recent progress of membranes with special wettability for oil-in-water emulsion separation

4.1 Stability of oil-in-water emulsion

The separation process of oil-in-water emulsions on or within the membrane is highly related to the stability of emulsion oil droplets. Understanding the interaction and stability mechanism of emulsion oil droplets in the emulsion is of significance for designing and developing more advanced membranes for separating emulsion. Shi et al. [51] investigated the interaction between two oil droplets in the water environment by carrying out droplet probe atomic force microscopy (AFM) (Fig. 4(a)). The interaction force between the oil droplets was directly measured and the stability of oil droplets in water was analyzed by combing the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [52, 53]. It was found that the stability of oil droplets is highly affected by the adsorbing of surfactant on the oil/water interface. As shown in Fig. 4(b), the coalescence phenomenon between two pure oil droplets was observed when reached a max interaction force of 0.6 nN in the absence of surfactants, which was induced by the attractive van der Waals force between two oil droplets. However, the coalescence among oil droplets can be largely hindered by incorporating a tiny amount of
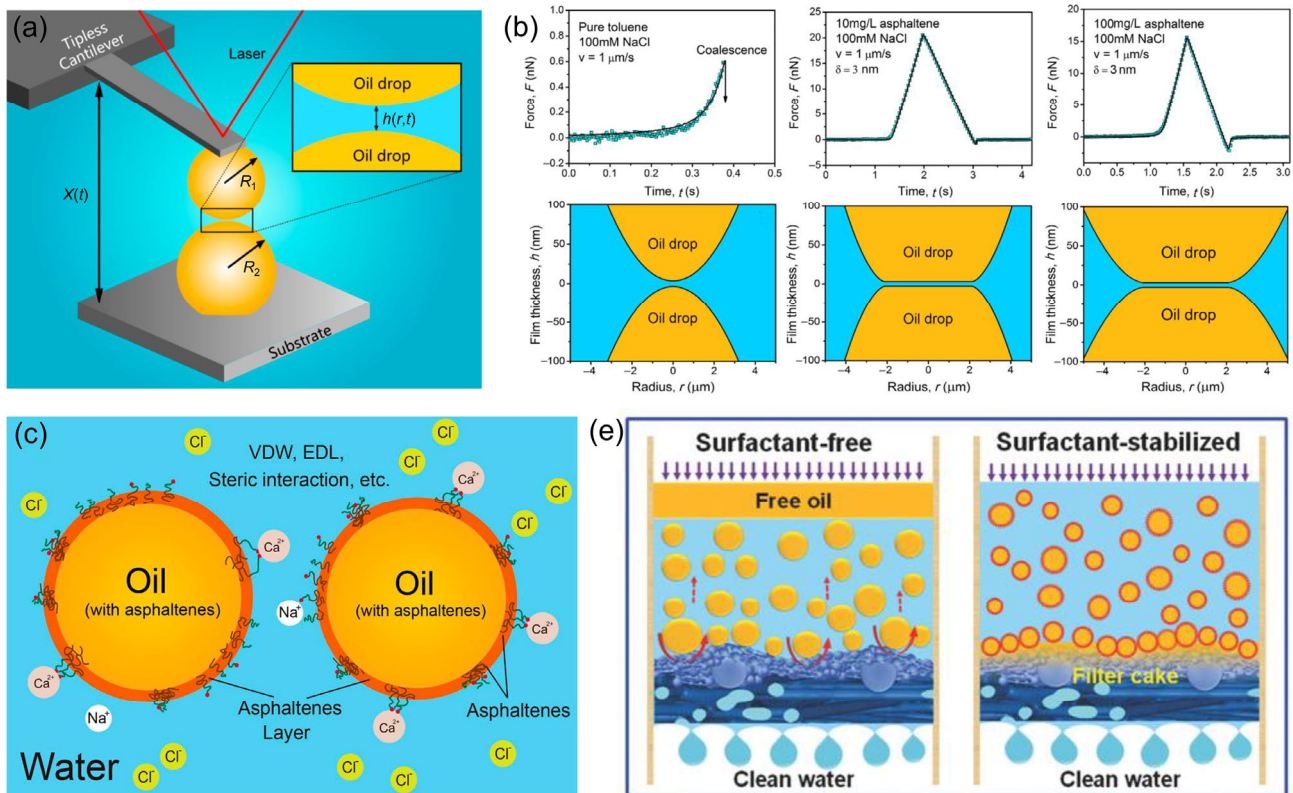
Fig. 4 (a) Schematic diagram of the experiment measuring the interaction force between underwater oil droplets using droplet probe AFM technique; (b) interaction force curves between oil droplets in a water environment containing different surfactant concentrations, and the corresponding droplet profile at the moment of maximum interaction force; (c) schematic of interactions between oil droplets in water [51]. Reproduced with permission from Ref. [51], © American Chemical Society, 2016. (d) Schematic diagram of surfactant-free oil-in-water emulsion and surfactant-stabilized oil-in-water emulsions on a filtration membrane [57]. Reproduced with permission from Ref. [57], © John Wiley & Sons, Inc., 2018.

surfactant (asphaltenes), which is because the repulsion force (e.g., electrostatic double layer interaction, steric interaction) between two oil droplets was tremendously promoted by the adsorbing of surfactant on the oil/water interface (Fig. 4(c)).

Oil-in-water emulsions are usually divided into two types depending on whether they contain a surfactant or not: surfactant-free oil-in-water emulsions and surfactant-stabilized oil-in-water emulsions. The surfactant-free oil-in-water emulsion is unstable and the emulsion oil droplets easily coalesced with the adjacent oil droplets to form larger oil droplets. On the contrary, the emulsion oil droplets in surfactant-stabilized emulsion hardly coalesce even if they were brought close under compression [54–56]. Therefore, the separation mechanism of the membrane for the surfactant-free oil-in-water emulsion and the surfactant-stabilized oil-in-water emulsion is fully different. As displayed in Fig. 4(d), the surfactant-free

oil droplets can form larger oil droplets by continuous coalescence and tend to detach from the membrane under the influence of buoyancy. However, the surfactant-stabilized oil droplets tend to transform into filter cakes and firmly block the membrane [57].

4.2 Superhydrophilic and superoleophobic membranes for separating oil-water emulsion

As discussed in Section 2, there are four factors regarded as keys for designing an oil/water separation membrane, that is, (1) suitable membrane pore; (2) high porosity; (3) low membrane thickness; and (4) superhydrophilic and superoleophobic properties. Factors (1)–(3) refer to the structural characteristics of the membrane and Factor (4) refers to the membrane wettability. From this point of view, the fabrication of oil/water separation membranes can be considered from two aspects: (1) directly endowing a suitable membrane with superhydrophilic and superoleophobic

features; (2) preparing a suitable membrane and subsequently endowing it with superhydrophilic and superoleophobic features. In this part, we summarized the recent developments of the superhydrophilic and superoleophobic membranes for separating oil-in-water emulsions, including the membrane fabrication methods, membrane separation performance, and working mechanism analysis.

4.2.1   Mesh membranes

As an inorganic porous material, metal mesh is an outstanding candidate for fabricating oil/water separation membranes, which is low cost, high strength, excellent durability, outstanding stability under severe conditions, and long-term preservation [58–60]. However, the pore of the commercially available metal mesh is usually too large to intercept the emulsion oil droplet. Zhang et al. [61] prepared a superhydrophilic and underwater superoleophobic $Cu(OH)_2$ nanowire-modified metal mesh by a chemical-based oxidation technology and took a first step to separate oil-in-water emulsions by using the as-prepared superwetting

metal mesh. The $Cu(OH)_2$ nanowires were formed on the copper mesh surface by the oxidation treatment of the commercial copper in the mixture solution of NaOH and $(NH_4)_2S_2O_8$. As shown in Fig. 5(a), the obtained $Cu(OH)_2$ nanowire copper mesh exhibited a water contact angle of nearly zero and an underwater oil contact angle of ~155°, demonstrating its special superhydrophilic and underwater superoleophobic properties. The adhesion force between the underwater oil droplet and the as-prepared copper mesh is less than 1 μN. The pore size of a 500 mesh copper mesh is reduced to less than 1 μm after constructing $Cu(OH)_2$ nanowire on its surface, which endowed it with the capacity to intercept emulsion oil droplets. The as-prepared copper mesh exhibited a flux of 500 L/(m²·h) for surfactant-free oil-in-water emulsion under solely gravity-driven and the oil contents in the collected filtrate were below 60 ppm.

Chen et al. [62] developed a superhydrophilic and underwater superoleophobic Co_3O_4 nanoneedle steel mesh by the combination of hydrothermal and calcination methods. As shown in Fig. 5(b), a dense
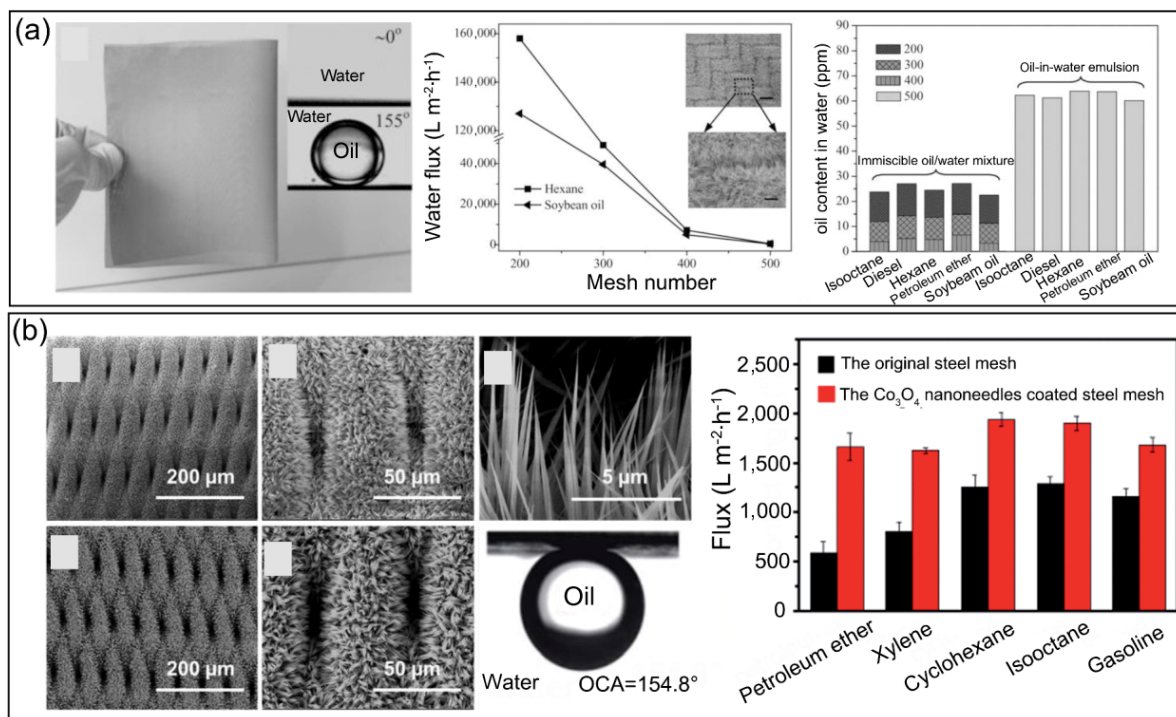

Fig. 5   (a) Optical appearance, wettability characterization, scanning electron microscope (SEM) images, and oil/water separation performance of the as-prepared superhydrophilic and underwater superoleophobic $Cu(OH)_2$ nanowire-copper mesh [61]. Reproduced with permission from Ref. [61], © John Wiley & Sons, Inc., 2013. (b) SEM images, wettability characterization, and oil/water separation performance of the as-prepared superhydrophobic and underwater superoleophobic Co_3O_4 nano-needle steel mesh [62]. Reproduced with permission from Ref. [62], Royal Society of Chemistry, 2016.

layer of Co_3O_4 nanoneedles with a length of 5 μm was grown on the mesh wires. The average pore size of the stainless-steel mesh was reduced from 16.3 to 4.6 μm after being coated with Co_3O_4 nanoneedles. Meanwhile, the wettability of the steel mesh changes from underwater oleophobic to superoleophobic. The as-prepared Co_3O_4 nanoneedles coated steel mesh showed fluxes of 160–340 L/(m²·h) for different surfactant-free oil-in-water emulsions at gravity-driven (1 kPa), and a high flux of ~2,000 L/(m²·h) at a negative pressure of 5 kPa. Additionally, the as-prepared steel mesh showed fluxes of 90–190 L/(m²·h) for the surfactant-stabilized oil-in-water emulsions under the drive of gravity. The separation efficiency of all surfactant-free and surfactant-stabilized oil-in-water emulsions was above 99%.

Besides, other surface modification methods including spraying-coating, spin-coating, electroplating, etc., and modification substances such as TiO_2, Al_2O_3, cement-alumina, etc., which have been developed to fabricate superhydrophilic and underwater superoleophobic metal meshes for separating oil-in-water emulsions. For example, $Cu(OH)_2$ nanoneedle modified-stainless-steel mesh [63], TiO_2 nanocluster-based mesh [64], cement-alumina coated mesh [65], $MnMoO_4$-coated copper mesh [66], and so forth [67–75].

4.2.2 Nanofibrous membranes

According to the Hagen–Poiseuille equation, an excellent filtration membrane for separating oil-water emulsions should be as thin as possible. Gao et al. [76] developed a photoinduced superwetting single-walled carbon nanotubes (SWCNT)/TiO_2 ultrathin network membrane for superfast filtration of oil-in-water emulsions. At first, the SWCNT network membrane was prepared by vacuum-filtering an SWCNT dispersion through a commercial cellulose ester filter membrane and subsequently separating it from the filter surface. Second, the SWCNT network membrane was coated with the tetra butyl titanate the precursor of TiO_2, and subsequently, sintering treatment at 400 °C for 4 h to obtain the SWCNT/TiO_2 nanocomposite membrane. As shown in Fig. 6(a), the thickness of the as-prepared SWCNT/TiO_2 membrane is around 60 nm and the pore diameter of the membrane ranges from 20 to 60 nm. The wettability of the as-prepared

SWCNT/TiO_2 membrane changed from hydrophilic (water contact angle of 82°) to superhydrophilic (water contact angle of ~0°) after UV-irradiation treatment for 1 h. The superhydrophilic characteristic of the as-prepared SWCNT/TiO_2 membrane can last for more than 3 days and recover to hydrophilic (water contact angle of 82°) after being stored in the dark for 7 days. Besides, the as-prepared SWCNT/TiO_2 membrane possesses an outstanding underwater superoleophobic and anti-oil adhesion property and the oil intrusion pressure of the membrane is around 6–7 kPa. The as-prepared membrane was used to treat both surfactant-free and surfactant-stabilized oil-in-water emulsions under 5 kPa of driving pressure. Moreover, the fluxes for a surfactant-free oil-in-water emulsion are 500–1,650 L/(m²·h) and the fluxes for a surfactant-stabilized oil-in-water emulsion are 750–900 L/(m²·h).

Electrospinning is a unique technology for manufacturing fiber membranes in which a polymer solution is jet-spun in a high-voltage electric field [77–79]. Electrospinning technology is regarded as a facile and effective way to fabricate nanofibrous membranes with tunable pore structures and adjustable surface wettability, showing great promise for meeting the requirements of oil-water separation membranes [80–85]. Ge et al. [57] developed a biomimetic and superwetting nanofibrous skin on a fibrous membrane by the combination of electrospraying and electrospinning technology (Fig. 6(b)). The as-prepared dual-layer membrane consists of a nanofibrous skin layer and a common polyacrylonitrile (PAN) nanofibrous layer. The PAN nanofibrous membrane with a thickness of ~100 μm and a mean pore diameter of 3.3 μm was fabricated first by the common electrospinning. In addition, the obtained PAN nanofibrous membrane possesses a maximum stress of 7.1 MPa, showing sufficient mechanical strength to be used as the substrate. Subsequently, an ultrathin skin layer (thickness of ~5 μm) was created on the PAN substrate by the electrospraying of a diluted PAN solution. The constructed skin layer is ultrathin and highly porosity (>90%) with sub-micrometer pores (average pore diameter of ~0.49 μm), which can effectively intercept the tiny emulsion oil droplets and simultaneously ensure the quick permeation of water. Moreover, the wettability
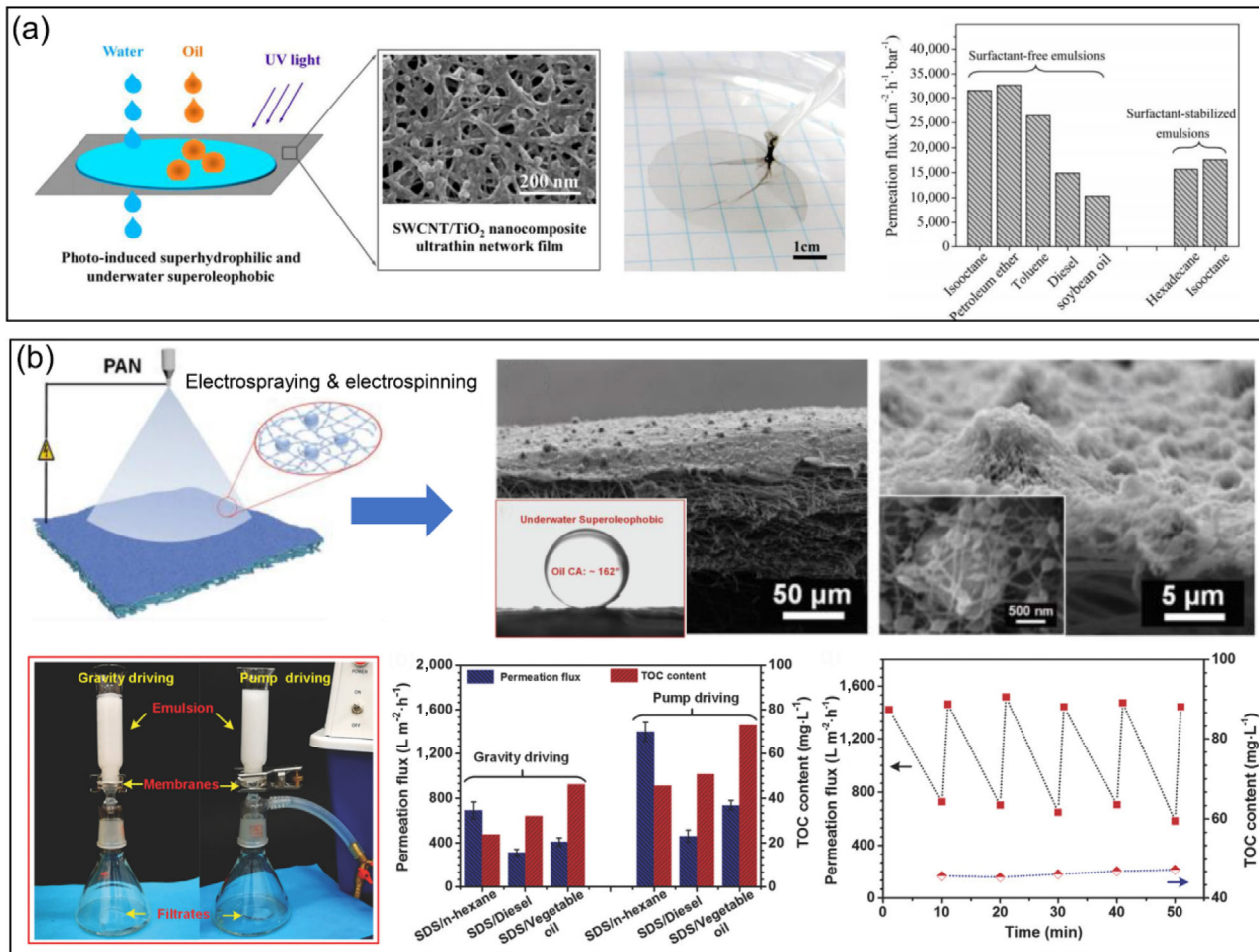
Fig. 6 (a) Schematic diagram, SEM image; optical appearance; and the oil/water separation performance of the SWCNT/TiO$_2$ nanocomposite network membrane [76]. Reproduced with permission from Ref. [76]. © American Chemical Society, 2013. (b) Schematic diagram of fabrication; SEM images; wettability tests; and oil/water separation performance of the electrospun superwetting nanofibrous membrane. Reproduced with permission from Ref. [57]. © John Wiley & Sons, Inc., 2018.

of the membrane was changed from underwater oleophobicity (oil contact angle of ~133°) to underwater superoleophobicity (oil contact angle of ~162°) by the hydrolysis treatment in NaOH solution. The as-prepared membrane exhibited excellent anti-fouling properties and high oil intrusion pressure beyond 22 kPa. The as-fabricated membrane showed good separation performance for both surfactant-stabilized and surfactant-free oil-in-water emulsions. Under the gravity-driven (diving pressure of~1 kPa), the filtration fluxes for various surfactant-free oil-in-water emulsions ranged from 1,900 to 5,200 L/(m^2·h) and ranged from 400–700 L/(m^2·h) for diverse surfactant-stabilized oil-in-water emulsions. Concerning the separation of surfactant-free emulsion, the emulsion oil droplets intercepted on the skin layer can coalesce and

demulsify to form free oil and eventually separate from the membrane surface under the fluence of buoyancy. However, when the emulsion was stabilized by the surfactants, the emulsion oil droplets were difficult to coalesce, which tended to form a filter cake on the surface of the membrane. This is why the filtration fluxes of surfactant-free oil-in-water emulsions were usually much higher than that of surfactant-stabilized oil-in-water emulsions. In conclusion, the permeation fluxes are increased with the increase of the external driving pressure. However, when the external pressure is too large, the tiny emulsion oil droplets would be forced to enter the membrane pores and block the channels inside the membrane, which result in a decline in permeation flux and separation efficiency.

Besides, many other superhydrophilic and underwater superoleophobic nanofibrous membranes have been fabricated for the separation of oil-in-water emulsions. For example, polydopamine (PDA) coated PAN nanofibrous membrane [86], silica/PVA nanofibrous membrane [87], PAN@ZIF-8 nanofibrous membrane [88], chitin nanofibrous membrane [89], PDA modified PTFE nanofibrous membrane [90], and so forth [91–95].

4.2.3 Commercial polymeric membranes

Commercial polymeric membranes are regarded as fundamental to membrane technology because of their advantages such as good flexibility, low cost, and easy operation [96]. However, common polymeric membranes such as polyvinylidene fluoride (PVDF), polysulfone (PSF), and cellulose acetate (CA) are usually hydrophobic and oleophilic, which results in the membranes being easily fouled by the oil while treating the oily wastewater [97–99]. Nowadays, to improve the anti-fouling property and oil/water filtration performance of polymeric membranes, many hydrophilization methods have been developed to give polymeric membranes with superhydrophilic and superoleophobic properties such as surface modifications, chemical grafting, and modified phase inversion [100–104].

Zhu et al. [105] prepared a superhydrophilic and superoleophobic PVDF membrane via surface grafting of a zwitterionic polyelectrolyte brush poly (3-(N-2-methacryloxyethyl-N, N-dimethyl) ammonatopropanesultone (PMAPS). The wettability of the original PVDF membrane with a static contact angle of ~130° was changed to ultra-hydrophilic with a contact angle of ~11° after PMAPS grafting. Besides, the water flux of the PMAPS grafted PVDF membrane increased sharply to 16,084 $L/(m^2 \cdot h \cdot bar)$ as compared to the original PDVF membrane in which no water permeation. As compared with the conventional hydrophilic polymer materials, the hydrogel coating is a desirable candidate for anti-oil-fouling modification for the membrane, which can form a stable hydration layer on the membrane. Yuan et al. [106] fabricated a hydrogel-tethered PVDF membrane with superwetting properties of superhydrophilic and underwater superoleophobic for separating oil-in-water emulsions

(Fig. 7(a)). As compared with the emulsion flux of 168 $L/(m^2 \cdot h \cdot bar)$ for the original PVDF membrane, the hydrogel-tethered PVDF exhibited a stable pure water permeation flux of ~2,000 $L/(m^2 \cdot h \cdot bar)$ and a surfactant-stabilized emulsion flux of ~900 $L/(m^2 \cdot h \cdot bar)$ after long-term recycle filtration.

However, the hydrogel layer is easy to be damaged and exfoliated from the membrane during the separation process because of its weak mechanical strength and ready swelling, which greatly limits its use in practical industry. Mo et al. [107] greatly improved the mechanical strength and durability of the hydrogel layer by constructing reinforcement hydrogel on the PAA-g-PVDF membrane. In their research, the hydrating ability and mechanical strength of the hydrogel layer were greatly enhanced by embedding the hydrophilic $Cu_3(PO_4)_2$ nanoparticles into the hydrogel layer (Fig. 7(b)). The separation tests of oil/water emulsions were performed by the cross-flow filtration equipment. The as-prepared $Cu_3(PO_4)_2$ composite hydrogel-coated PAA-g-PVDF membrane exhibited strong oil-repellency with nearly 100% recovery of flux during the cyclic separation of surfactant-stabilized oil-in-water emulsions. To address the contradiction between the high adhesion of hydrogel to the membrane and its repellency to oil, Gao et al. [108] developed a gradient adhesive hydrogel decorated PVDF membrane for separating oil/water emulsions (Fig. 7(c)). The composite hydrogel consists of an inside-out gradient distribution of hydrated polymer (calcium alginate (CaAlg)) and adhesive polymer (protocatechuic acid (PCA)). Moreover, the innermost PCA is used to ensure the hydrogel layer can firmly immobilize the membranes and the outermost CaAlg is used to protect membranes from oil pollution. The as-prepared gradient hydrogel decorated PVDF membrane exhibited excellent anti-oil-fouling ability for various light and viscous oil, as well as outstanding separation performance and recycling performance of approximately 100% flux recovery for crude oil-water mixture (layered) and surfactant-stabilized oil-in-water emulsions.

4.2.4 Other porous membranes

Recently, other types of porous materials such as fabric [109], wood [110], particles [111], and so forth,
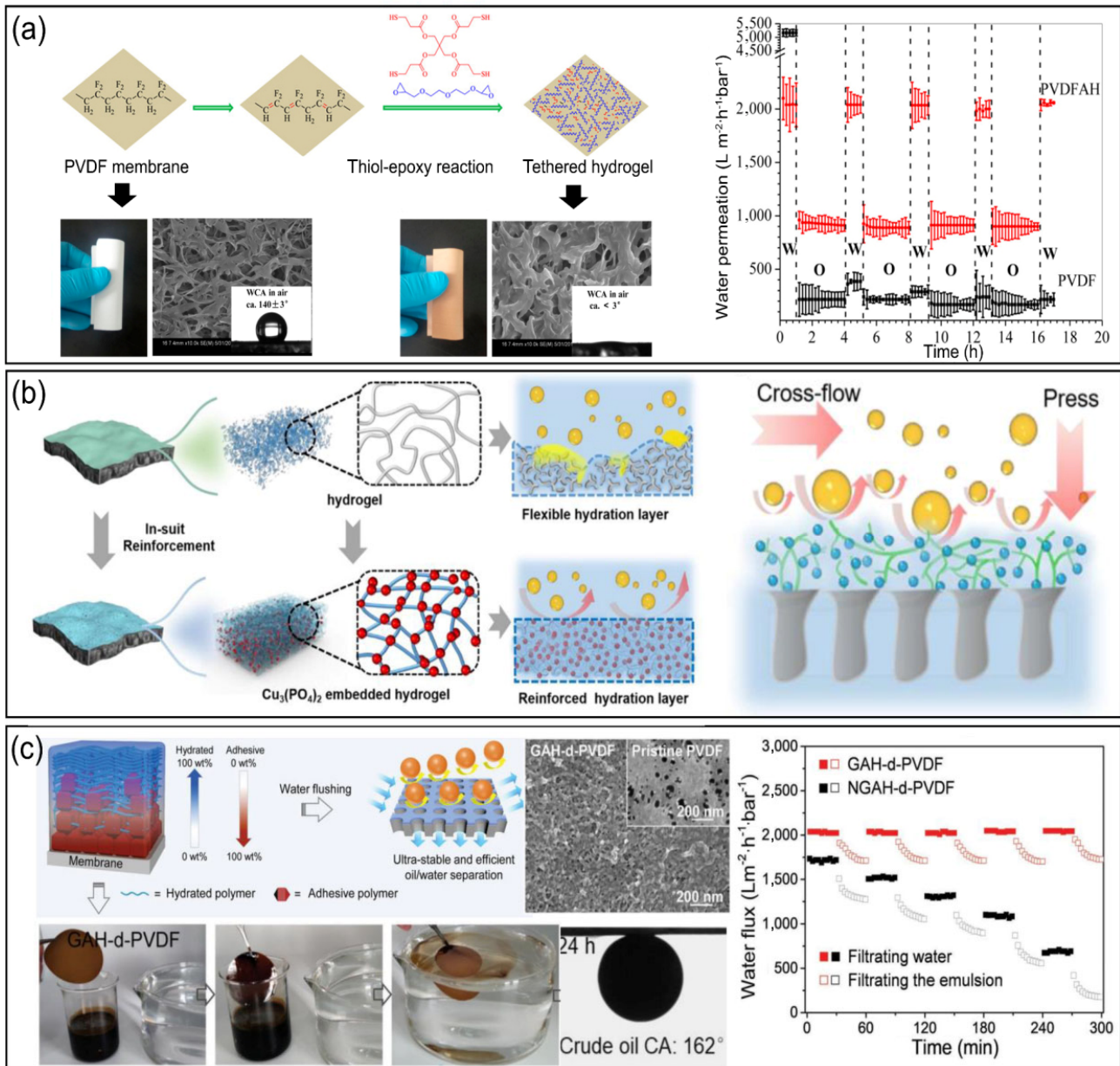
Fig. 7 (a) Scheme of the fabrication process; optical appearance; SEM images; and oil/water separation performance of a hydrogel-tethered PVDF membrane [106]. Reproduced with permission from Ref. [106], © American Chemical Society, 2015. (b) Scheme illustration of the fabrication process of the $Cu_3(PO_4)_2$ nanoparticles reinforced hydrogel-modified PVDF membrane for oil/water emulsion separation [107]. Reproduced with permission from Ref. [107], © American Chemical Society, 2022. (c) Scheme of the fabrication process; SEM images; anti-oil-fouling tests; and oil/water separation performance of a gradient adhesive hydrogel decorated membrane [108]. Reproduced with permission from Ref. [108], © John Wiley & Sons, Inc., 2022.

have been broadly developed and applied as a filter for separating oil-in-water emulsions. Wood with natural pore structures is a green, degradable, cheap, and abundant material, which can be applied as a substitute for polymeric and metal membranes for separating oil/water mixtures. Natural wood with pores diameters >50 μm is invalid for separating

oil-in-water emulsion because of its relatively large pores. Kim et al. [112] fabricated a wood membrane with a pore size <10 μm for efficiently separating oil-in-water emulsions (Fig. 8(a)). The pits in the longitudinal–tangential plane of the wood were opened after removing the lignin and hemicellulose via chemical treatment, which led to the formation of

massive small pores and the enhancement of the flexibility of the wood membrane. The obtained wood membrane with superhydrophilic and superoleophobic properties can efficiently separate surfactant-stabilized oil-in-water emulsions and exhibited a permeation flux of 460.8 L/(m²·h) and a separation efficiency of 99.43% under the action of a driving pressure of 5 kPa. Some inorganic particles with superwetting properties such as sand grains, aluminum particles, and so forth, were assembled as a filter for the separation of oil-in-water emulsions. Kong et al. [113] developed a particle-packing filter consisting of superhydrophilic Al₂O₃ particles for the effective separation of both oil-in-water emulsions and water-in-oil emulsions (Fig. 8(b)). Furthermore, Yao et al. [114] fabricated a UiO-66 decorated polyester fabric membrane with superhydrophilic and underwater superoleophobic properties by *in situ* growing HPAA-modified UiO-66 crystals and used it for separating oil-in-water emulsions. Moreover, Zhang et al. [115] prepared a TiO₂ nanorod-modified ceramic membrane with superhydrophilic and underwater superoleophobic property for reducing the degree of

surface fouling of ceramic membrane and enhancing it separation efficiency for oil-in-water emulsions. Besides, Zeng et al. [116] endowed the filter paper with underwater superoleophobic property by using the surface modification of polyvinyl alcohol and tolylene diisocyanate, and applied it for effective separation of oil-in-water emulsions.

4.3 Demulsification membranes for separation of oil–water emulsion

The accumulation of emulsion oil droplets on or within membrane pores usually results in a sharp decline of permeation flux, which leads to frequent cleaning needed by the "size-sieving" membrane and a severe challenge in the long-term continuous treatment of oily wastewater. Recently, some demulsification-type membranes with asymmetric wettability were fabricated to destabilize the oily emulsions and directly capture the emulsion oil droplets, which breaks through the pore size limitation of the "size-sieving" membrane and opens a new insight into the efficient and continuous treatment of oil-in-water emulsions. Yang et al. [117] developed a Janus cotton
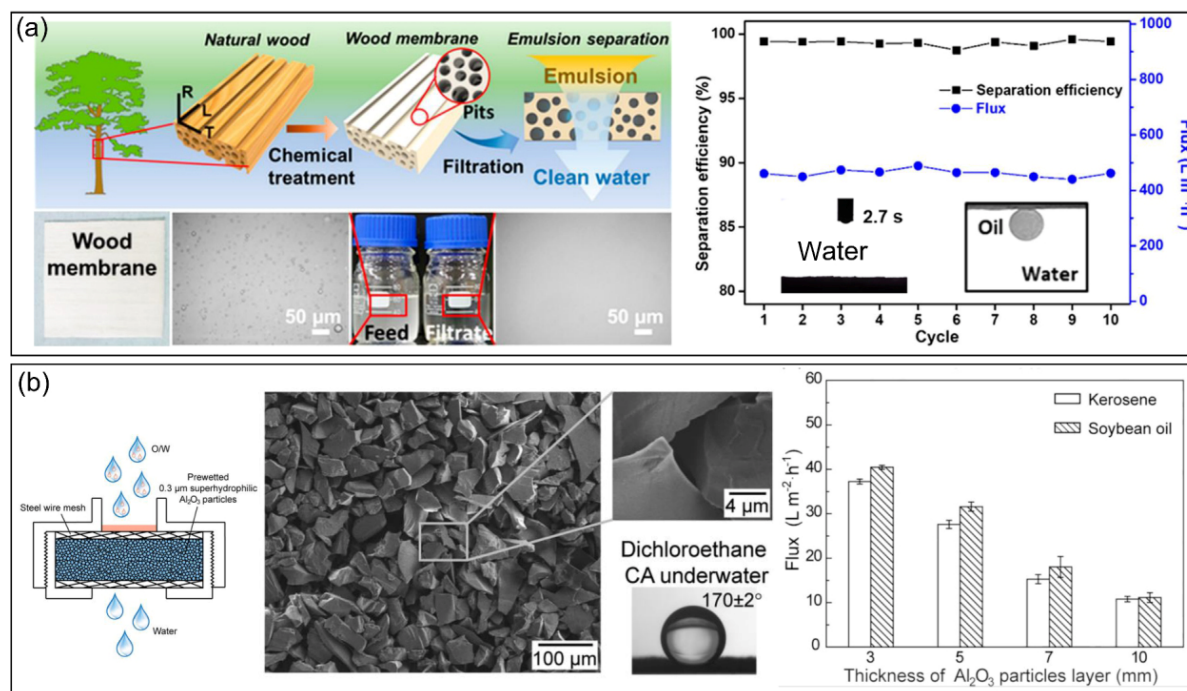

Fig. 8 (a) Schematic illustration of the fabrication process; optical images; and oil/water separation performance of a wood membrane [112]. Reproduced with permission from Ref. [112], © American Chemical Society, 2020. (b) SEM images, wettability tests, and schematics of the experimental set-ups for oil/water separation based on the Al₂O₃ particles-based filter [113]. Reproduced with permission from Ref. [113], © American Chemical Society, 2020.

fabric with larger sizes to separate emulsion oil droplets from diverse oil-in-water emulsions (Fig. 9(a)). The as-prepared Janus fabrics are superhydrophilic on one side and superhydrophobic on the other. When the hydrophilic side of the Janus fabrics face oil/water emulsions, only the oil droplets can enter the fabric pores and eventually permeate through the fabric. Wang et al. [118] *in situ* monitored the demulsification and unidirectional transportation process of emulsion oil droplets on a Janus membrane by carrying out a laser scanning confocal microscope (Fig. 9(b)). The results showed that the emulsion oil

droplet rapidly disappeared on the hydrophilic side of the Janus membrane, which evidenced that the oil droplet was transported from the hydrophilic side to the hydrophobic side, thus achieving the effective demulsification of oil-in-water emulsions.

Inspired by the desert beetles that could capture tiny water from fog, Li et al. [119] developed a biomimetic membrane with a similar surface to the desert beetle's back (Fig. 9(c)). The as-prepared membrane consists of hydrophobic/oleophilic bumps assembled on an underwater superoleophobic nanofibrous membrane. When the oil-in-water emulsion
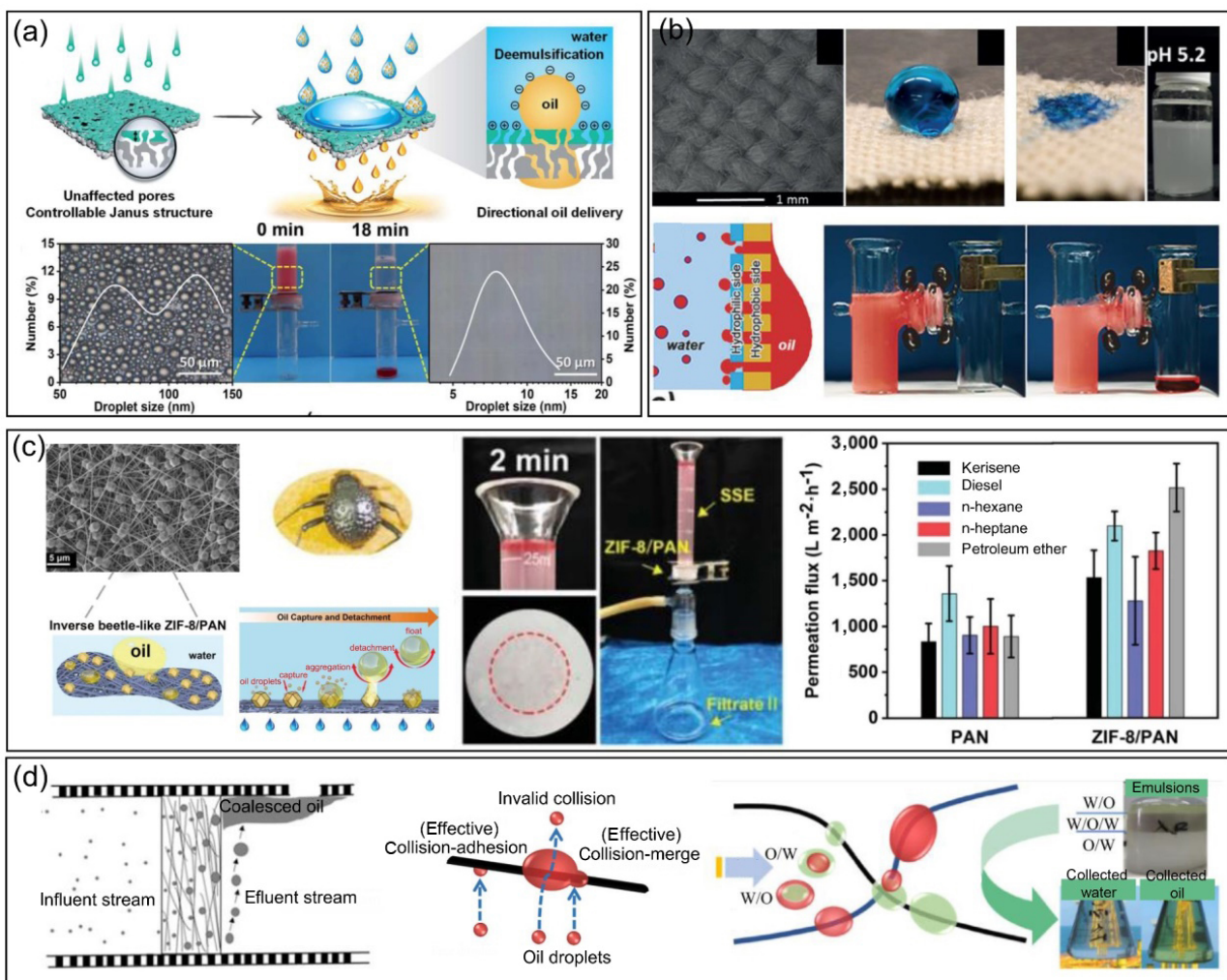

Fig. 9 (a) Separation of emulsion oil from oil-in-water emulsions based on a Janus cotton fabric [117]. Reproduced with permission from Ref. [117], © Royal Society of Chemistry 2019. (b) Schematic illustration of the construction process and oil/water separation performance of demulsification-type Janus membranes [118]. Reproduced with permission from Ref. [118], © John Wiley & Sons, Inc., 2016. (c) Schematic description, oil/water separation performance of the desert beetle-like nanofibrous membrane [119]. Reproduced with permission from Ref. [119]. © Royal Society of Chemistry 2021. (d) Fibrous coalescence filtration in treating oil-in-water emulsions [120–122]. Reproduced with permission from Ref. [120–122]. © SAGE Publications, 2021; © Elsevier B.V., 2021; and © SciEngine, 2021.

permeated through the membrane, the emulsion oil droplets were captured by the oleophilic bumps and merged into larger oil droplets, finally detaching from the membrane. As compared with the conventional superhydrophilic and underwater superoleophobic membranes, the oleophilic bumps can induce the emulsion oil droplets to aggregate and demulsify, thus exhibiting greater oil/water separation performance. The filtration flux of the PAN membrane for surfactant-stabilized oil-in-oil emulsion was increased from 1,358 to 2,514 L/(m^2·h) after the introduction of the oleophilic bumps.

To realize the continuous and long-term separation of oil-in-water emulsions, some fibrous coalescence bed filters have been developed. Two basic mechanisms were proposed to understand the coalescence filtration of emulsion oil droplets through the fibrous bed filter: surface coalescence and depth coalescence [120]. In surface coalescence, the oil droplets that are larger than the pore diameter of the fibrous bed would be intercepted by the filter instead of passing through it. The intercepted emulsion oil droplets on the surface of the membrane gradually coalesce with the incoming oil droplets, and finally form an oil film on the surface of the filter. In in-depth coalescence, the oil droplets smaller than the pore size of the fibrous bed would enter the membrane pore under the driven continuous water phase [123]. The entered oil droplets would be captured by the fibers, merge with the neighboring oil droplets, grow bigger, and eventually drain out the fibrous filter (Fig. 9(d)). The separation performance of fibrous coalescence bed membrane is mainly affected by the bed parameters including fiber diameter, pore size, porosity, fiber wettability, and bed height. These factors should be carefully considered when designing a fibrous coalescence bed membrane. It was found that the fibers possessing suitable hydrophobic-oleophilic properties are greatly beneficial for enhancing the capture and coalescence of oil droplets. Yang's group [121, 122, 124–126] developed a novel fibrous coalescer consisting of weave hydrophilic and oleophilic heterogeneous fibers for continuous separation of oil-in-water emulsions. Moreover, the hydrophilic fibers can promote the permeation efficiency of the water phase and the oleophilic fibers can promote the coalescence efficiency of emulsion oil droplets. The as-prepared fiber coalescer was successfully applied for wastewater treatment in real offshore platforms. The oil concentration in the collected discharge water is only 25 mg/L, which meets the international effluent discharge standards limits of 45 mg/L. Besides, the outlet oil concentrate of the fibrous coalescer remains below 40 mg/L after even one year of continuous treatment. This new technology shows great prospects in practical industrial applications such as offshore gas fields, oil extraction, and so forth.

5 Conclusions and outlook

Membrane technology has become an outstanding solution strategy for the treatment of oily wastewater (oil-in-water emulsions) because of its exclusive advantages of low cost, high efficiency, easy operation, and eco-friendliness. In this review, we have summarized the recent developments in membranes with special wettability for separation oil-in-water emulsions, which includes the mechanism analysis of emulsion separation membrane, membrane fouling issues, and design strategy of membrane for enhancing its anti-oil-fouling ability and emulsion separation performance. The membrane separates oil-in-water emulsion by intercepting the emulsion oil droplets. However, the membrane is easily blocked and fouled by the intercepted oil droplets, resulting in a sharp decline in permeation flux and limiting its continuous and long-term use. Tunning the membranes with special wettability e.g., superhydrophilic and superoleophobic can greatly enhance the permeability of the continuous water phase and inhibit the fouling of oil droplets, thus promoting the separation performance and anti-oil-fouling ability of membrane for oil-in-water emulsions. Currently, various materials and methods have been developed for fabricating superhydrophilic and superoleophobic membranes. The developments in fabrication methods, main materials, and oil/water separation performance were summarized.

Although many advanced membranes for separating oil-in-water emulsions have been successfully developed, many challenging issues still exist and need to be solved urgently in the future. First, the

membrane surface with micro/nanostructures and a hydrated layer are crucial for enhancing its anti-oil-fouling performance. However, the mechanical strength of the structure of the membrane surface is usually weak and easily damaged. Second, due to the "size-sieving" membrane separating emulsions based on an interception mechanism, the membrane can only intercept the emulsion oil droplets larger than the membrane pores. However, real oily wastewater is complex and contains emulsion oil droplets ranging from hundreds of nanometers to tens of micrometers, which requires the membrane pores to be small enough to ensure interception efficiency. In turn, the permeability of the water phase will be greatly limited. Therefore, how to design and optimize the membrane parameters e.g., pores, porosity, and surface structures is still a challenge. Finally, even though some demulsification fibrous membranes were reported and applied for treating real oily wastewater in practical industry, the dynamic capture and coalescence mechanism of emulsion oil droplets within the fibrous beds are still unclear. In future work, revealing the detained dynamic behaviors of emulsion oil droplets within the fibrous membrane is of significance for optimizing the emulsion separation performance of demulsification membranes.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article. The author Zhiguang GUO is the Editorial Board Member of this journal.

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