This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Huang, Shilin; Ras, Robin H.A.; Tian, Xuelin
Antifouling membranes for oily wastewater treatment

Published in:
Current Opinion in Colloid and Interface Science

DOI:
[10.1016/j.cocis.2018.02.002](https://doi.org/10.1016/j.cocis.2018.02.002)

Published: 01/01/2018

Document Version
Peer reviewed version

Please cite the original version:
Huang, S., Ras, R. H. A., & Tian, X. (2018). Antifouling membranes for oily wastewater treatment: Interplay between wetting and membrane fouling. *Current Opinion in Colloid and Interface Science*, 36, 90-109.
<https://doi.org/10.1016/j.cocis.2018.02.002>

Accepted Manuscript

Antifouling membranes for oily wastewater treatment: Interplay between wetting and membrane fouling

Shilin Huang, Robin H.A. Ras, Xuelin Tian

PII: S1359-0294(17)30174-7
DOI: doi:[10.1016/j.cocis.2018.02.002](https://doi.org/10.1016/j.cocis.2018.02.002)
Reference: COCIS 1180

To appear in:

Received date: 5 January 2018
Accepted date: 7 February 2018

Please cite this article as: Shilin Huang, Robin H.A. Ras, Xuelin Tian , Antifouling membranes for oily wastewater treatment: Interplay between wetting and membrane fouling. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Cocis(2018), doi:[10.1016/j.cocis.2018.02.002](https://doi.org/10.1016/j.cocis.2018.02.002)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Antifouling membranes for oily wastewater treatment: interplay between wetting and membrane fouling

Shilin Huang¹, Robin H. A. Ras^{2,3*}, Xuelin Tian^{1*}

¹School of Materials Science and Engineering, Key Laboratory for Polymeric Composite & Functional Materials of Ministry of Education, Sun Yat-sen University, Guangzhou 510006, China

²Aalto University, School of Science, Department of Applied Physics, Puumiehenkuja 2, 02150 Espoo, Finland

³Aalto University, School of Chemical Engineering, Department of Bioproducts and Biosystems, Kemistintie 1, 02150 Espoo, Finland

Email: tianxuelin@mail.sysu.edu.cn, robin.ras@aalto.fi

Abstract

Oily wastewater is an extensive source of pollution to soil and water, and its harmless treatment is of great importance for the protection of our aquatic ecosystems. Membrane filtration is highly desirable for removing oil from oily water because it has the advantages of energy efficiency, easy processing and low maintenance cost. However, membrane fouling during filtration leads to severe flux decline and impedes long-term operation of membranes in practical wastewater treatment. Membrane fouling includes reversible fouling and irreversible fouling. The fouling mechanisms have been explored based on classical fouling models, and on oil droplet behaviors (such as droplet deposition, accumulation, coalescence and wetting) on the membranes. Membrane fouling is dominated by droplet-membrane interaction, which is influenced by the properties of the membrane (e.g., surface chemistry, structure and charge) and the wastewater (e.g., compositions and concentrations) as well as the operation conditions. Typical membrane antifouling strategies, such as surface hydrophilization, zwitterionic polymer coating, photocatalytic decomposition and electrically enhanced antifouling are reviewed, and their cons and pros for practical applications are discussed.

Keywords: oily wastewater, membrane, fouling, wettability, emulsion

1. Introduction

Oily wastewater, which can cause extensive pollution to water and soil, is produced from various sources, e.g., from oil/gas recovery, metal finishing, mining, transportation and oil refining, et al.[1-15] Some oily substances (e.g., phenols, petroleum hydrocarbons and polyaromatic hydrocarbons) are toxic and can inhibit the growth of plants and animals. To human beings they also bring mutagenic and carcinogenic risks. Direct disposal of the oily wastewater is forbidden by government regulations,[16, 17] and oils in the oily wastewater should be removed to meet the discharge standard (i.e., the highest acceptable concentration of oil/grease in the wastewater is typically in the range of 5-42 ppm depending on the country and location of the platform).[3,

18-22]

Generally, oily wastewater contains oils in different forms, including free-floating oils, unstable dispersed oils and stable emulsified oils.[11, 13, 17, 23] Unlike free-floating oils (e.g., spilled oils on the ocean), dispersed oils are randomly distributed in water. The dispersed oils have a strong tendency to coalesce and spontaneously evolve into free-floating oils. In contrast, emulsified oils are rather stable due to the presence of surfactants (or surface-active molecules acting similar to surfactants, e.g., asphaltenes in crude oil). Emulsified oils have small droplet sizes, typically smaller than 10 μm . [4, 8, 13, 17, 23, 24] They are commonly found in produced water from oil/gas recovery and metal finishing industries.[11]

Conventional methods to separate oily wastewater include skimming, sedimentation, centrifugation, dissolved gas flotation and biological methods.[16, 17, 21, 23] Though these methods can be used for treating free-floating oils and dispersed oils, most of them are not suitable for treating emulsified oils because the emulsified oils have small droplet sizes, low density difference compared to water ($< 150 \text{ kg/m}^3$) and high stability.[11, 17, 23, 25, 26] Membrane filtration provides a highly desirable method for treating oily wastewater containing emulsified oils due to its energy efficiency, ease of processing, and low maintenance cost.[14, 18, 23, 27, 28]

Membrane separation of oily wastewater is basically based on two effects, size exclusion (i.e., sieving) and selective wettability.[5-7, 9, 10] The first effect means that the membrane allows water to pass through under an applied pressure while blocks the oil droplets which are larger than the membrane pores. [29] The second effect guarantees that the oil droplets do not wet and permeate the membrane through its selective wetting properties towards water and oil (e.g., hydrophilicity and underwater oleophobicity).[5, 6, 30-33]

Depending on the pore size and separation mechanism, membrane filtration can be divided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). [4, 29] Polymers and ceramics are generally used to fabricate filtration membranes. Polymer membranes are relatively cheap, while ceramic membranes have high mechanical strength, high resistance to harsh environments and long lifetime.[34, 35] Other porous materials, such as metal meshes, textile, nanofiber mats and foams can also be used for pretreatment of oily wastewater. [36-45]

Although membranes with different pore sizes and materials are commercially available, they are susceptible to fouling when used for oil/water separation.[46] Fouling leads to continuous decline of flux over time and severely decreases the efficiency of filtration. When the membranes are badly fouled, physical cleaning (e.g., water flush and backflush) or/and chemical cleaning methods have to be performed.[1, 4, 18, 21, 41, 47-50] Fouling leads to higher operation cost and shortens the lifespan of the membrane, impeding the wide applications of membrane technology in oily wastewater treatment.[51]

2. Fundamentals of membrane fouling

2.1 Classification of fouling

Generally speaking, membrane fouling is caused by complicated interactions between components in the feed solution and the membrane, which are related to their physicochemical properties.[52] Fig. 1 illustrates the change of permeate flux (i.e., volumetric flow rate of permeate per unit of membrane area, L/m^2h) during treatment of oily wastewater using membrane.[53-56] In region I ($t_0 \rightarrow t_1$), when pure water is used as the feed, the flux of pure

water J_0 depends on the size of the membrane pores, the porosity and the applied pressure (as described by Darcy's law). In region II ($t_1 \rightarrow t_2$), the oily wastewater is filtrated. The flux $J(t)$ declines overtime due to the fouling of the membrane (at t_2 the flux decreases to J_1). The membrane fouling can be either reversible or irreversible. The reversible fouling refers to the fouling that can be cleaned up by simple physical methods, such as water flush or backflush.[22, 30, 57, 58] In region III ($t_2 \rightarrow t_3$) of Fig. 1, when water is reused as the feed to wash the membrane, the flux can be recovered to J_2 . The fouling that can be recovered by physical cleaning is reversible fouling ($J_{\text{rev}} = J_2 - J_1$). In contrast, the fouling that cannot be recovered by physical cleaning is called irreversible fouling ($J_{\text{irrev}} = J_0 - J_2$).[30] The cleaning up of irreversible fouling requires more intense methods, e.g., using chemicals or applying thermal treatments.[21, 53] Once the irreversible fouling becomes serious, the membrane modules have to be replaced.[14]

Compared to reversible fouling which can be mitigated by optimizing the operation conditions, irreversible fouling is more relevant to the surface chemistry and structure of the membranes. In the following section, the fouling models in wastewater treatment will be discussed.

Fig. 1 Permeate flux during filtration of pure water (region I), oily wastewater (region II) and again pure water (region III).

2.2 General fouling models

2.2.1 Resistance-in-series model

The general form of the resistance-in-series model, given in Eq. (1), can be used to quantify the contribution of each fouling mechanism to the flux decline during filtration:[52, 53, 59-62]

$$J = \frac{\Delta P}{\mu(R_m + R_{\text{rev}} + R_{\text{irrev}})}$$

Eq. 1

where J is the permeate flux, ΔP is the cross-membrane pressure, and μ is the viscosity. The resistances R_m , R_{rev} and R_{irrev} are the hydraulic resistance of the fresh membrane, the hydraulic resistances due to reversible and irreversible fouling, respectively.[62, 63] The reversible fouling resistance R_{rev} is removable by physical means, e.g., by backflush or switching the feed to pure water.[58] The irreversible fouling resistance R_{irrev} reflects the deposition of material on the membrane that cannot be removed by physical cleaning.

The resistance-in-series model provides a method to quantify the reversible and irreversible

fouling during filtration. R_{rev} and R_{irrev} normally increase quickly at the beginning of filtration, but slow down during long-time operation. For operation at constant pressure, a steady state (constant R_{rev} and R_{irrev}) may be reached if there is a balance between the accumulation of foulants and their removal away.[3, 23, 63] Note that R_{rev} and R_{irrev} are also dependent on the operation conditions (e.g., applied pressure, flow velocity, and physical cleaning methods). Eq. (1) also implies that a higher applied pressure can lead to the increase of permeate flux. However, membrane fouling may become more serious at a higher pressure. Thus, during oily wastewater treatment, it is necessary to optimize the operation conditions in order to obtain a high permeate flux and meanwhile prevent serious membrane fouling.

2.2.2 Hermia's fouling models

Membrane fouling depends on the size of foulant (either solid or liquid), foulant-membrane and foulant-foulant interactions. Hermia's fouling models are widely used to describe the flux decline (i.e., fouling) during membrane filtration.[62, 64] These models include complete blocking model, standard blocking model, intermediate blocking model and cake filtration model. In complete blocking model, each foulant particle blocks a pore of the membrane without superimposition upon each other, thus the blocked surface area is proportional to the permeate volume. In standard blocking model, the size of the particle is smaller than the pore diameter. As a result, the pollutant particles can enter the pores and deposit on the pore walls, leading to the reduction of the pore's volume which is proportional to the permeate volume.[62] In intermediate blocking model, it is assumed that not all foulant particles are in direct contact with the pores, but some of them sit on top of others. In the cake filtration model, large amounts of foulant particles accumulate on the membrane and form a cake layer, which creates an additional resistance to the permeate flow. These models predict different decline trends of permeate flux during filtration. They have been employed in analyzing the experimental results in oily wastewater treatment using membranes.[13, 28, 35, 59, 65]

In these fouling models, the foulant particles which enter the pores of the membrane or strongly adsorb on the membrane surface can contribute to irreversible fouling. Otherwise, they can be easily washed away and contribute to the reversible fouling.

For oily wastewater treatment, membrane fouling is expected to be more complicated than the classical Hermia's fouling models. First, oil droplets may wet the membrane surface and the pores. Second, oil droplets accumulating on the membrane can deform and coalesce during filtration. These specific behaviors which significantly influence membrane fouling during oily wastewater treatment will be discussed in details below.

3. Fouling mechanisms in oily wastewater treatment

3.1 Fouling of membrane by oil

Fig. 2 Illustration of an oil droplet under water sitting on top of a porous membrane.

Wetting behavior of oil droplet on membrane. Fig. 2 shows an oil droplet in direct contact with the membrane under water. The membrane has an intrinsic underwater contact angle θ_{ow} larger than 90° . In this sketch the oil droplet is sitting on top of an idealized pore (i.e., cylindrical pore with vertical sidewalls).[3] The oil droplet can cross the membrane when the applied pressure is larger than the critical pressure (P_{crit}). Following Nazzal and Wiesner,[66] P_{crit} can be calculated using Eq. 2 (Eq. 2 is slightly different from that given in the original paper of Nazzal and Wiesner because of a typographical error, as noted by Cumming et al.[67]):

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

Eq. 2

where γ_{ow} is the interfacial tension between oil and water, and θ is the contact angle measured from the water side, i.e., $\theta = 180^\circ - \theta_{ow}$ (see Fig. 2). r_{pore} and r_{drop} are radii of the pores and oil droplets, respectively.

Several conclusions can be drawn from Eq. 2. First, the underwater oil contact angle θ_{ow} determines the sign of P_{crit} . For $\theta_{ow} < 90^\circ$, P_{crit} is negative, implying that the oil can wet and fill the pores of the membrane spontaneously even under zero pressure. The filtration may fail because the oil can easily pass through the membrane. Thus, θ_{ow} should be larger than 90° to obtain successful filtration, and is preferred to be considerable higher since it allows a high transmembrane operation pressure, which is important to increase the permeate flux.

Second, when θ_{ow} is $> 90^\circ$, the critical pressure increases with decreasing pore radius. This means that membranes with smaller pores have higher rejection efficiency to oil droplets.

Lastly, Eq. 2 also indicates that larger droplets have a higher critical pressure, and thus smaller droplets are easier to pass through the pores under pressure. Obviously, if the droplets are smaller than the pore size, the droplets would freely pass through the membrane pores, leading to failure of filtration. For droplets of infinite large size (e.g., an oil film covering the membrane), the critical pressure becomes $P_{crit} = 2\gamma_{ow} \cos \theta / r_{pore}$. [68]

Oil fouling models. During filtration of oily wastewater, emulsified oil droplets are carried towards the membrane following the permeate flow and then deposit on the membrane surface. The deposited droplets would block partially the membrane pores at the early stage of filtration (Fig. 3a). With prolonged filtration time, more and more oil droplets accumulate on the membrane surface, leading to the formation of cake layer (Fig. 3b). In crossflow filtration (in such filtration mode the feed flow travels tangentially across the membrane surface), as the crossflow could also carry oil away from the cake layer, a steady cake layer is expected to form once a balance between oil deposition and oil removal is reached, as noted before. Since oil droplets are deformable, the resultant cake layer can be densely packed and shows high resistance to water permeation.[8] Oil droplets in the cake layer are thermodynamically unstable and tend to coalesce.[69] In some experiments, it was found that coalescence led to formation of larger oil droplets which were easier to remove by crossflow.[3, 8] This can be understood by considering the critical penetration pressure of oil droplets. Larger droplets have higher critical pressure (see

Eq. 2), thus they are less likely to permeate through the membrane and more probable to be carried away by the crossflow (the critical droplet size beyond which the oil droplet can be carried away by crossflow has been predicted based on the force balance on the droplet).[3] In this respect, coalescence of oil droplets helps to mitigate membrane fouling.

However, if severe pressure is exerted on the oil droplets, they may experience a wetting transition on the membrane (especially for less oleophobic membranes), accompanying significant decrease of their oil contact angles under water. [11] These collapsed oil droplets might coalesce laterally on/within the membrane, and consequently a contiguous oil film forms (Fig. 3c). It is expected that the contiguous oil film forms more easily on membranes which are underwater oleophilic. [8] Such contiguous oil film obviously brings serious membrane fouling.

For droplets smaller than or comparable to the pore size of membrane, droplets could enter or be forced into the pores by the permeate flux. This leads to internal oil fouling within the pores (Fig. 3d), also a type of membrane fouling that is difficult to clean. [3, 8]

Fig.3 Different oil fouling models in oily wastewater filtration. (a) Oil droplets partially blocking the membrane pores. (b) Cake layer formation on the membrane. (c) Contiguous oil film on the membrane. (d) Oil droplets within the membrane pores.

3.2 Controlling factors of membrane fouling in oily wastewater treatment

Effect of surface chemistry. As discussed in the previous section, one controlling factor of membrane fouling is the affinity between oil droplets and the membrane under water (i.e., underwater oleophilicity/oleophobicity). Oil droplets with high affinity to the membrane can wet the membrane and permeate into the pores, leading to serious fouling. Thus, a poor affinity between oil and membrane under water (i.e., underwater oleophobicity) is a requisite for achieving antifouling membrane. Considering that a membrane with higher hydrophilicity shows higher underwater oleophobicity,[70, 71] hydrophilic membranes can be chosen for antifouling purpose.

Effect of pore size. The pores should be sufficiently small in order to have a good size-sieving effect as well as to prevent “standard pore blocking”. From a practical point of view, however, the pores should not be too small, otherwise the membrane resistance to permeate flux would be

too high.

Effect of surface structure. The surface roughness influences the membrane fouling on two respects. On the one hand, due to the hydrophilicity of the membrane, water can be trapped in the micro-/nanoscale rough structure. Oil droplets in contact with the membrane are in fact contacting a composite interface with a high portion of water, which could bring extremely low adhesion to oil.[37, 72-76] On the other hand, it is widely reported that increasing the roughness leads to higher fouling tendency due to the accumulation of oil at the valley of the rough surface.[1, 23, 52, 61, 77-80] It seems that the effect of surface roughness on membrane fouling is dependent on the size of oil droplets in respect to the characteristic length of the roughness. If the oil droplets are significantly larger than this characteristic length, an underwater superoleophobic state which decreases fouling tendency can be obtained. On the contrary, if the oil droplets are small compared to the roughness, they could be trapped at the valley of the rough surface, leading to accumulation of oil and membrane fouling.

Effect of surface charge. Oil droplets and membranes can carry surface charges under water. It is generally accepted that if the membrane and the oil droplets have different surface charges, the electrostatic attraction would promote membrane fouling, and vice versa. [58, 79, 81] This electrostatic attraction/repulsion between the oil droplets and the membrane can be estimated based on the classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.[82] It is also reported that surface charges can influence membrane fouling by modifying its wettability towards oil droplets.[83]

Effect of surfactants. Surfactants are generally present in oily wastewater.[16, 30, 74, 84, 85] Their influence on membrane fouling during wastewater treatment is multiple.[11, 13, 18, 22, 86, 87] First, surfactants can be adsorbed on/in the membrane and increase its resistance to water permeation (especially for UF and NF membranes since they have small pores), and the surfactant micelles may also block the pores leading to flux decline.[11] In this respect, surfactants act as foulants during membrane filtration.

Second, surfactants can alter the wetting behavior of oil droplets on the membrane.[13] A hydrophilic membrane may become less hydrophilic and more oleophilic upon adsorption of surfactants, and vice versa.[88] This is because the hydrophilic (polar) end groups of surfactants would preferentially adsorb onto the hydrophilic membrane surface, whereas the hydrophobic hydrocarbon chains are likely to be exposed outwards. Consequently, the contaminated hydrophilic membrane becomes prone to be fouled by oils (i.e. showing less antifouling capability). Meanwhile, the membrane would also lose its selective wettability towards oil and water upon surfactant adsorption, which also adversely influence its efficiency in oil-water separation.

Interestingly, a recent study by Schutzius et al.[89] showed that water-soluble surfactants with concentration above the critical micelle concentration (CMC) could impart high underwater oil contact angles (larger than 150°) for a wide range of surfaces, such as glass, aluminum, poly(methylmethacrylate) and poly(vinylidene fluoride), irrespective of their intrinsic wetting properties. They suggested to use such effect (i.e. the detergency effect) for oil/water separation, though the use of high-concentration surfactants may cause environmental concern. [90]

In addition, surfactants decrease the oil/water interfacial tension. This effect facilitates the deformation of oil droplets and their permeation through the pores (since the critical penetration pressure decreases, see Eq. 1), which could adversely influence the separation efficiency.

At last, surfactants (being anionic or cationic) impart charges on the oil droplets. The attractive (or repulsive) electrostatic forces between the membrane and oil droplets would increase (or decrease) membrane fouling tendency, as discussed in the previous section. Lu et al., however, reported an unusual phenomenon: irreversible fouling was alleviated when the charge of surfactant-stabilized oil droplets was opposite to the ceramic membrane during UF.[13, 22] This phenomenon was explained by the synergetic steric effect and demulsification effect.[13] The steric effect meant that at the beginning of filtration, some surfactants were adsorbed on/in the membrane due to electrostatic attractions. The adsorbed surfactants acted as barriers for oil penetration. The demulsification effect meant that, as surfactants became less available to stabilize oil droplets (because some of them were adsorbed on the membrane), oil droplets close to the membrane became unstable and tend to coalesce (demulsify). Because the coalesced droplets were more likely to be rejected by the membrane, the irreversible fouling was alleviated.

Effect of salts. Oily wastewater often contains certain amount of salts, which also influences membrane fouling during filtration.[1] First, salts can change the oil-water interfacial tension, influencing droplet deformation and penetration through the membrane.[11] Second, salts may promote droplet coalescence due to electrostatic screening. This also influences membrane fouling. Moreover, antifouling membranes may gradually lose their antifouling property under saline water because of the decomposition and corrosion of hydrophilic components of the membrane.[72, 91] At last, during treatment of saline wastewater the membranes can also be contaminated by salt crystals.[2, 50]

Effect of operation conditions. Operation conditions also influence membrane fouling.[1, 17, 34, 63, 90, 92] The filtration module should be designed to have appropriate hydrodynamic conditions to mitigate fouling.[26] For example, the crossflow configuration shows less fouling compared to the dead-end configuration.[18, 74] Using pulsated feed flows or other perturbations at the membrane surface (e.g., applying continuous or pulsated electric fields) can also efficiently decrease membrane fouling. [34] Since more concentrated oily wastewater is more prone to foul the membrane,[51] it is helpful to perform pretreatments (e.g., using flocculation or pre-filtering to decrease oil concentration) before filtration.[1, 38, 51]

4 Methods of testing fouling

Direct measurement of the flux decline during filtration is a standard method of quantifying fouling. When membranes with sufficient optical transparency in the wet state are used, the fouling dynamics can be directly observed under optical microscope (in-situ method).[3] Ex-situ methods, such as scanning electron microscopy (SEM)[13, 17, 22, 24, 49, 50, 93] and atomic force microscopy (AFM)[2] provide nanoscopic routes to observe the fouled membranes. The macroscopic fouling phenomenon, i.e., oil stain on the membrane, can also be utilized to test the fouling property of the membrane qualitatively.[40, 94]

When an oil droplet approaches and retracts from the membrane surface, a low adhesion force is indicative of low fouling tendency. This adhesion force can be recorded using a force tensiometer,[31, 76, 83, 85, 95, 96] which has a force resolution in the sub-micro-Newton range. For nano-Newton resolution, AFM could be used since it can serve as a powerful method to study the molecular forces between the oil droplet and the solid substrate (e.g., membrane).[82]

5 Antifouling strategies

5.1 General method: improving surface hydrophilicity

It is normally true that a more hydrophilic substrate is more oleophobic under water.[70, 71] As membranes with higher underwater oleophobicity are more resistive to oil fouling, a general method of preparing antifouling membrane is to improve the hydrophilicity of the membrane.[17, 22, 24, 28, 40, 53, 60, 77, 79, 94, 97-100] In addition, a hydration layer may form on the surface of some hydrophilic materials (such as zwitterionic polymers, polyelectrolytes and polyethylene glycol) under water.[24, 30, 101-105] This hydration layer prevents oil from directly contacting the membrane and thus decreases the fouling tendency. There are various methods to improve the hydrophilicity of the membrane, including surface modification, blending and fabricating nanocomposite membranes. [17, 23, 30, 32, 52, 54, 57, 59, 72, 74, 75, 77, 80, 90, 97, 98, 106-113]

Surface hydrophilization. The surface hydrophilicity of a membrane can be increased by surface modification, e.g., introducing hydrophilic polymers or nanoparticles on the membrane surface.[98] Hydrophilic polymers can be introduced to the membrane surface by either surface grafting or coating.[32] Surface grafting requires functional groups on the membrane surface, so that the hydrophilic polymers with reactive groups can be grafted to it via formation of chemical bonds.[30, 54, 74] In comparison, surface coating does not require functional groups on the membrane,[17, 52, 57, 72, 75, 80, 107-110, 114] and the polymers are coated on the membrane by strong physical adsorption. The stability of the coating can be further improved by crosslinking.[40, 115] In addition to hydrophilic polymers, hydrophilic nanoparticles (e.g., metal oxide nanoparticles) are also used to coat the membrane surface to improve the surface hydrophilicity.[97, 111] Surface modification has the advantage of low cost, as it can be easily adopted to modify various commercial membranes.

Generally speaking, surface hydrophilicity is improved by introducing polar groups on the membrane. However, once the polar groups are exposed to air or oil, they tend to orient inward, minimizing the surface energy, see the illustration in Fig. 4 for poly(acrylic acid) (PAA) and poly(sodium, 4-styrenesulfonate) (PAS) decorating surfaces. [116] The surface hydrophilicity may degrade due to such surface reconstruction. Recently, Huang and Wang developed self-cleaning surfaces with stable surface hydrophilicity by coating the surfaces with cellulose nanofibrils (CNFs).[116] The cellulose nanofibrils had a unique isotropic core-corona configuration, which showed a polar corona with uniformly, densely and symmetrically arranged surface carboxyl and hydroxyl groups, and a core with crystalline nanocellulose strands (Fig. 4, left illustration). This configuration enabled large number of polar groups pointing towards the environment, allowing stable surface hydrophilicity.

Fig. 4 Illustration of the projections of the molecular structural units of cellulose nanofibril (CNF, left), poly(acrylic acid) (PAA, middle), and poly(sodium, 4-styrenesulfonate) (PSS, right). MAS is the abbreviation of model anionic surface. CNF orients the identical number of carboxyl and

hydroxy groups to water and air or oil as a result of its isotropic core-corona configuration, while PAA and PSS orient the ionic groups preferentially to water and the hydrophobic moieties to air or oil owing to the anisotropic configuration. Reproduced with permission from John Wiley and Sons.[116]

Membranes with underwater superoleophobicity (i.e. underwater oil contact angle $> 150^\circ$) have been widely studied in recent years. Once wetted by water, these membranes can efficiently repel oil and show excellent antifouling property. Underwater superoleophobicity is usually obtained by combining hydrophilic chemical composition and micro/nanoscale roughness on the membrane surface.[19, 37, 74, 76, 101, 115, 117, 118] Due to the intrinsic rough surface structures, membranes are in fact expected to exhibit underwater superoleophobicity once their surfaces are effectively hydrophilized. A number of methods, such as hydrogel coating and salt-induced phase-inversion approach have been employed to fabricate membranes with underwater superoleophobicity.[19, 31, 102, 115, 117, 119, 120] For example, Gao et al. reported a polyionized hydrogel coated copper mesh (underwater oil contact angle $\sim 165^\circ$), which exhibited ultralow adhesion to viscous crude oils under an aqueous environment and could effectively separate a crude oil/water mixture with high flux and high oil rejection. [100]

Blending and fabricating nanocomposite membranes. Surface modification only imparts a thin hydrophilic layer on the membrane surface (also on the walls of the pores). Therefore, the long-term stability of the resulting hydrophilic surface is relatively poor.[112] This problem can be solved by incorporating hydrophilic materials in the membrane through blending or/and fabricating nanocomposite membranes. For blending, copolymers with hydrophilic components are blended with the membrane matrix.[59, 77, 90] For fabricating nanocomposite membranes, hydrophilic nanoparticles (e.g., metal oxides, graphene oxide, etc.) are dispersed into the membrane matrix for membrane preparation.[23, 47, 52, 56, 94, 98, 111, 113, 121, 122]

5.2 Zwitterionic coating

Zwitterions are neutral molecules with equal numbers of positively and negatively charged functional groups. Zwitterionic polymers, which have zwitterionic functional groups in every repeating unit of the polymer, are highly resistant to oil fouling.[32, 54, 75, 81, 105, 109, 110, 123] Their fouling resistance comes from the fact that they superiorly bind water molecules via electrostatically induced hydration.[103] Different from other hydrophilic polymers (e.g., polyethylene glycol, PEG) which can only form a hydration layer via hydrogen bonding, the zwitterionic polymer forms a hydration layer via strong electrostatic interactions due to the strong dipole moments in the zwitterionic units.[104, 105] Molecular dynamics simulations showed that for $-N^+(CH_2)_2SO_3^-$ sulfobetaine there were about 7 water molecules around a sulfonate group and 19 water molecules around a quaternary ammonium group.[124] The tightly immobilized hydration layer at the zwitterionic polymer-water interface has been detected using, for example, sum-frequency-generation vibrational spectroscopy and low-field nuclear magnetic resonance.[103, 104, 125, 126] Wu et al. revealed that there were about 8 water molecules tightly bound with one sulfobetaine zwitterion unit for poly(sulfobetaine methacrylate) modified surface.[104] The tightly bound water layer at the surface of zwitterionic polymer forms a barrier for oil fouling. For more details about the antifouling mechanisms of zwitterionic polymers, readers are referred to Ref. [127].

He et al. grafted zwitterionic poly(2-methacryloyloxyethyl phosphorylcholine) brushes on solid substrates, and the resulting surface was underwater superoleophobic.[103] As the surface was rather flat, the underwater superoleophobicity was not due to surface roughness, but solely due to the intrinsic hydration layer on the zwitterionic polymer surface. The resultant surface exhibited complete oil repellency when it was wetted by water. In the dry state, as expected, the zwitterionic surface could be easily fouled by oil. However, once the fouled surface was immersed in water, the oil spontaneously detached from the surface, see Fig. 5a. Such intrinsic oil repellency of zwitterionic polymer under water is rather unique. In contrast, most underwater superoleophobic surfaces with micro/nanoscale hierarchical structures are difficult to maintain the underwater superoleophobicity once contaminated by oil.[103, 116] Underwater superoleophobic surfaces based on polyelectrolyte grafting also cannot be re-wetted by water if they are pre-wetted by oil, because when in contact with oil the polyelectrolyte surfaces reorient their ionic groups inwards to lower the surface free energy, leading to the loss of surface hydrophilicity.[82, 103]

Fig. 5 (a) Time-lapse photos taken after immersion of 60 μL canola oil fouled substrate in water. The substrate is grafted with zwitterionic poly(2-methacryloyloxyethyl phosphorylcholine) brushes. Reprinted with permission from [103]. Copyright 2015 American Chemical Society. (b,c) Measured (open symbols) and calculated (red curves) interaction forces of zwitterionic poly(3-[dimethyl(2-methacryloyloxyethyl) ammonium] propanesulfonate) (PMAPS) with an oil droplet in water (b) and with a water droplet in oil (c). Positive and negative interaction forces represent repulsive and attractive forces between the droplet and substrate, respectively. The arrow in (c) indicates attachment of the water droplet on PMAPS surface. Open circles are force data measured during approach, and solid triangles are force data measured during retraction. Adapted with permission from John Wiley and Sons.[82]

Shi et al. measured the force between an oil droplet and a zwitterionic polymer surface under water using AFM (Fig. 5b),[82] and no obvious attraction and adhesion forces were detected when the oil droplet approached and retracted from the surface, respectively. Surprisingly, when a water drop approached the zwitterionic polymer surface under oil, as shown in Fig. 5c, a

long-range “hydrophilic” attraction was observed. It was attributed to a strong dipolar interaction between the water droplet and the zwitterionic polymer surface.

As a promising strategy, zwitterionic polymers have been used to fabricate membranes with complete resistance to irreversible fouling (either by blending or grafting).[14, 103] Kaner et al. [14] showed that increasing the zwitterionic content in the additive copolymer (containing zwitterionic components) did not always result in improved membrane performance. During membrane formation via non-solvent induced phase separation, the additive copolymer with high zwitterion content (51-52 wt%) led to macrophase separation from the membrane matrix, leading to a poor membrane performance. On the contrary, with appropriate copolymers that contained 18-19 wt% zwitterionic monomer, membranes with high permeate flux and remarkable fouling resistance were obtained even with very small amounts of additive copolymer.[14]

5.3 Combining fouling-resistant and fouling-release mechanisms

Several groups have reported enhanced antifouling property of membranes by combining fouling-resistant and fouling-release mechanisms.[18, 55, 95, 128-132] In the fouling-resistant mechanism, water molecules are tightly bound to the hydrophilic surface and form a hydration layer, preventing oil from contacting the surface. In the fouling-release mechanism, the surface is covered by low-surface-energy fluorine atoms, which reduces the adhesion energy between oil and the surface and facilitates the release of adsorbed oil. [131, 132]

Fig. 6 (a) Time-dependent permeate fluxes for hybrid membranes in three-stage filtration: 0.5 h water filtration, 1 h oil-in-water emulsion filtration and 0.5 h water filtration after rinsing. Top: the -CF₃ groups are grafted in the PVDF matrix. Bottom: -CF₃ groups are introduced on the TiO₂ particles. The results show that the antifouling property of the membrane is improved by increasing -CF₃ content. (b) Schematic of collaborative defense mechanisms for heterogeneously

constructed hybrid membranes. Hydrophilic TiO_2 components contribute to the fouling-resistant mechanism, $-\text{CF}_3$ groups contribute to fouling-release mechanism. Adapted with permission from Royal Society of Chemistry. [132]

Zhao et al. fabricated polyvinylidene fluoride (PVDF) based hybrid membranes using in-situ biomimetic mineralization and non-solvent induced phase separation.[132] The resulting surfaces, as reported by the authors, had both inorganic hydrophilic components TiO_2 (facilitating formation of hydration layer) and organic low-surface-energy components ($-\text{CF}_3$). The low-surface-energy components ($-\text{CF}_3$) were either anchored on the TiO_2 surface or grafted to the PVDF matrix. The surface energy decreased with $-\text{CF}_3$ content, while the oil fouling resistance was significantly enhanced, see Fig. 6a. The proposed mechanism is shown in Fig. 6b. The hydrophilic TiO_2 contributed to the fouling resistance mechanism, while the $-\text{CF}_3$ groups on the membrane surface contributed to the fouling release mechanism.

Wang and Lin integrated low-surface-energy perfluoroalkyl functional groups into membranes with chitosan based hydrogel surface.[95] The resulting membranes showed excellent anti-fouling property when treating crude-oil-in-water emulsions, as long as the perfluoroalkyl functional groups were not excessive on the surface.[95] It was postulated that the low-surface-energy moieties in the hydrogel surface promoted the release of foulants by local hydrodynamic perturbation. However, as noted by the authors, there is still no direct proof regarding such mechanism either by experiments or simulations.[95] Since overabundance of low-surface-energy functional groups has a negative effect on the antifouling property, there might be an intermediate concentration of low-surface-energy functional groups at which the best antifouling property can be obtained. However, such optimized condition has not been systematically studied yet.

While the combination of fouling-resistant and fouling-release mechanisms has been qualified as a potential antifouling strategy, further understanding and verification of such antifouling mechanism is still needed. It is also important to develop a criterion for designing such antifouling surfaces if possible.

5.4 Photocatalytic cleaning

Generally speaking, if the membrane is irreversibly polluted by oil or other organic compounds in the feed solution, chemical cleaning or high-temperature decomposition should be applied to clean the membrane.[48-50] This cleaning process takes extra time and operation costs. Using photocatalytic nanoparticles such as TiO_2 and ZnO , it is possible to prepare membranes with self-cleaning properties.[84] Under UV light or sunlight, photocatalytic nanoparticles are able to generate highly reactive species like superoxide anions and hydroxyl radicals to decompose the organic contaminants.[43, 133] This provides a remote-controlled and non-stop antifouling strategy.[43, 48, 133-136]

For example, Li et al. fabricated a multifunctional underwater superoleophobic porous membrane by growing anodized hierarchical TiO_2 nanotubes on the surface of porous titanium.[84] They demonstrated that once the membrane was contaminated by octadecyltrimethoxysilane, it lost its superhydrophilicity. However, after the illumination of UV light the superhydrophilicity was recovered. In addition to the self-cleaning property, the membranes with photocatalytic functionality had the ability to decompose toxic water-miscible

organic molecules when water flowed through the membrane.[84]

As this strategy requires illumination of UV light or sun light,[133] the filtration module needs some special designs, e.g., using transparent windows for light transmission. It is also important to ensure that the polymer membranes themselves are not decomposed by the photocatalytic activity.

5.5 Electrically enhanced antifouling

During filtration, the foulant particles (e.g., oil droplets and other foulants) flow to the membrane and form the cake layer. For charged particles, this convective flow can be compensated by applying an electric field, which drives the charged particles away from the membrane and prevents the formation of cake layer. The effect of using an electric field to change the trajectories of charged particles is called electrophoresis, which has been used to mitigate membrane fouling during filtration of wastewater. The electric field can be applied either across the membrane, or using the membrane as an electrode. [137]

For example, Geng and Chen developed antifouling tubular Al_2O_3 microfiltration membranes, with the inner layer modified by Magnéli Ti_4O_7 which was conductive.[138] The resulting conductive inner layer of the membrane was connected to a direct current (DC) electric field and acted as anode. Meanwhile, a stainless steel wire located at the center of the tubular membrane acted as cathode (see Fig. 7 for the schematic of the electrically-assisted membrane filtration module). The model oily wastewater was a peanut-oil-in-water emulsion stabilized by hexadecyltrimethylammonium bromide (CTAB), thus the oil droplets were positively charged. Thanks to the electrophoresis, the antifouling performance as well as the permeate quality were significantly improved when the electric field was applied.

Fig. 7 Schematic diagram of the electrically-assisted antifouling filtration process. (1) DC power supply, (2) annular permeate compartment, (3) inner layer modified $\text{Ti}_4\text{O}_7/\text{Al}_2\text{O}_3$ composite membrane, (4) wire electrode, (5) permeate side pressure gauge, (6) retentate compartment, (7) retentate side pressure gauge, (8) flowmeter, (9) pressure control valve, (10) discharge valve, (11) feed solution reservoir, (12) metering pump, (13) back pressure valve, (14) pulsation damper, (15) inlet pressure gauge, and (16) permeate reservoir. Reproduced with permission from

Elsevier.[138]

Apart from electrophoresis, the electrochemical reactions can also be used to improve antifouling performance during filtration. Li et al. adopted a coal-based carbon membrane as the anode for treating sodium dodecyl sulfate (SDS) stabilized fuel-oil-in-water emulsion. As the oil droplets were negatively charged, it was expected that the oil would easily foul the membrane which acted as anode. However, the antifouling performance of the filtration system was improved under an electric field. This unexpected phenomenon was believed to be related to the electrochemical reactions taking place at the anode (membrane). The reactive intermediates (e.g., $\cdot\text{OH}$, $\text{HO}_2\cdot$, and H_2O_2) on the membrane surface efficiently decomposed and removed oil droplets from the surface.[93]

The electrically enhanced antifouling strategy avoids use of chemicals, consumes low energy and is straightforward for handling. Yet, it has the following issues. First, the electrophoretic mobility of charged particles would be significantly reduced when the feed contains salts (due to electrostatic shielding).[138] This restricts the wide application of electrically enhanced antifouling strategy in oily wastewater treatment since many oily wastewater streams contain salts.[137] Second, it is necessary to finely control the applied voltage for the antifouling mechanism based on electrochemical reactions. Otherwise if the voltage is too high, bubbles can form on the surface of membrane and block the pores, leading to decrease of the permeate flux.[93, 137] At last, if oppositely charged particles are present in the oily wastewater, the charged membrane might attract the particles resulting in unwanted blocking of membrane pores.

5.6 Hydrophilic dynamic membranes

Typically, improving the hydrophilicity of membranes requires complicated physical or chemical processes, e.g., surface modification, blending and fabricating nanocomposite membranes. Alternatively, it can be easily realized by using hydrophilic dynamic membranes. A hydrophilic dynamic membrane is formed by in-situ filtering a coating solution containing either inorganic or organic hydrophilic particles through a supporting membrane.[139] The resulting deposited layer of hydrophilic particles (Fig. 8a) acts as a hydrophilic filtration membrane, which isolates pollutants and protects the supporting membrane from fouling (Fig. 8b). The dynamic membrane shows additional resistance to permeate flux depending on the size of particles (larger particles form dynamic membranes with smaller resistances).[58] As the particles in the dynamic membrane are not chemically connected to each other or to the supporting membrane, they can be easily removed by backwash (Fig. 8c). Therefore, the fouling on the dynamic membrane is reversible. Moreover, after backwash a fresh dynamic membrane can be regenerated by depositing another hydrophilic particle layer. In a word, dynamic membranes have the benefits of simple preparation, easy removal and regeneration. [58, 139]

Fig. 8 Hydrophilic dynamic membranes for antifouling. (a) The dynamic membrane, i.e., the deposited layer of hydrophilic particles (red spheres), can be fabricated by filtering a coating solution containing hydrophilic particles through a supporting membrane. (b) The hydrophilic dynamic membrane traps foulants (e.g., the oils, indicated by yellow spheres) and protects the supporting membrane from fouling. (c) The particles and foulants in the dynamic membrane can be easily removed by backwash (indicated by arrow). Re-drawn from Ref. [58].

Under a dead-end filtration condition, Lu et al. used hydrophilic Fe_2O_3 particles with an average particle size of 780 nm to fabricate dynamic membrane on an ultrafiltration ceramic membrane.[58] The use of relatively large particles for the dynamic membrane avoided pore blocking on the supporting membrane and guaranteed a small resistance of the dynamic membrane. If Fe_2O_3 particles were pre-coated on the supporting ceramic membrane before treating the oil-in-water emulsion, the fouling of the ceramic membrane was significantly reduced. The authors also pointed out that at a neutral pH condition, the electrostatic attractions between the membrane and the Fe_2O_3 particles helped to stabilize the dynamic membrane. However, at an alkaline condition (e.g., pH=8), the dynamic membrane and the ceramic membrane showed repulsive forces, facilitating the removal of fouled Fe_2O_3 particles by alkaline water. This mild cleaning condition avoided the use of strong alkaline (pH > 10) and high temperature ($\sim 80^\circ\text{C}$) backwash which could cause severe corrosion to the filtration system.

The strategy using dynamic membranes for antifouling also has some drawbacks. It increases the resistance to permeate flux and requires more investments on the equipment (e.g., the reservoir containing particle solutions should be installed). Moreover, extra efforts should be made to collect, clean and recycle the polluted particles which are washed away by backwash. It is also necessary to optimize the operation conditions for deposition and filtration, in order to have a stable dynamic membrane which prevents oil from contacting the supporting membrane.

5.7 Magnetic Pickering emulsions for fouling-free separation

Dudchenko et al. pointed out that underwater superoleophobic membranes did not completely resist fouling under realistic conditions, especially when the oil concentration in the oily wastewater was high.[140] They suggested using Pickering emulsions to decrease fouling during UF. In this strategy, magnetic nanoparticles (diameter ~ 600 nm) were mixed with the oily water to form a Pickering emulsion (oil droplets were stabilized by nanoparticles). The nanoparticles located at the droplet surface efficiently prevented oil droplets from contacting the membrane and thus mitigated membrane fouling by oil. Because the UF membrane had a small pore size, only water passed the membrane while the emulsified oils and nanoparticles were

blocked. When this strategy was used to treat oily water with large quantity of crude oil (10%), a minimal fouling tendency was observed. Thanks to the magnetic property of the magnetic nanoparticles, continuous oil-water separation may be possible following the proposed procedures in Fig. 9. [140]

Fig. 9 Complete oil emulsion treatment system: starting from the top left, oily water enters a mixer with Fe_3O_4 particles to form a Pickering emulsion; the Pickering emulsion enters the UF system, where an oil-free permeate stream and a concentrated Pickering emulsion stream are produced; the concentrated Pickering emulsion is passed through a magnetic separator, which separates water and Fe_3O_4 particles from oil, producing an oil stream and Fe_3O_4 particle slurry that is reused for the formation of a new Pickering emulsion (brown dots are Fe_3O_4 particles and large yellow dots are oil droplets). Adapted with permission from [140]. Copyright 2015 American Chemical Society.

This antifouling strategy requires that the nanoparticles have a high affinity to the oil-water interface which can be quantified by the detachment energy U_d (the energy required to remove the particle from the interface):[141]

$$U_d = \pi R^2 \gamma (1 \pm \cos \theta_w)^2, \quad (2)$$

where R is the radius of the particle, γ is the interfacial tension between oil and water, and θ_w is the contact angle of the nanoparticles at the oil-water interface measured from the water side. The sign in the bracket is negative (or positive) if the particle is removed from the interface to the water (or oil) phase. Eq. 2 implies that a high detachment energy demands a high oil-water interfacial tension and a contact angle near 90° (if $\theta_w > 90^\circ$, the particles may detach from the oil side).

If surfactants are present in the system, the interfacial tension γ decreases leading to a low detachment energy. In this case, it is difficult to fabricate stable Pickering emulsions. Therefore, the antifouling strategy based on magnetic Pickering emulsions only works effectively in the absence of surfactants. In addition, in order to recover and reuse the magnetic particles, complex post-processing (e.g., magnetic separation and wicking steps) is required,[140] which would increase the operation costs.

5.8 Other antifouling strategies

Liquid-based gating mechanism for antifouling membranes. Hou et al. proposed an

antifouling strategy based on liquid-based gating mechanism (Fig. 10).[142] The pores of the membrane were infused by a low-free-energy liquid, which completely sealed the pores and formed a coating layer. A transport liquid (or gas) which had a lower affinity to the membrane must deform the pore-filling liquid interface in order to enter and penetrate the pores. The critical pressure required for the penetration depended on the interfacial tension between the infusion liquid and the transport liquid. As different transport liquids had different critical pressures, it was possible to separate the liquids by adjusting the operation pressures. In addition, because the transport liquids were only in contact with the infusion liquid, the solid membrane was not fouled by the transport liquids. This anti-fouling strategy was successfully applied to separate air/water/oil mixtures.[142] If such liquid-infused membrane is used to treat oily wastewater, it is not clear whether the infusion liquid would bring undesired effect such as contaminating the filtrate (i.e., water). Moreover, it might be difficult to treat oily wastewater containing surfactants or other organic compounds, because they could alter the surface wettability of the membrane by adsorption and influence the infusion of the gate-forming liquid.

Fig. 10 Liquid-based gating mechanism. If the pore is filled with a stably held liquid (green), flow of gas and liquid will be gated by pressure-induced deformation of the gating liquid surface. When the pressure is higher than the critical pressure ($P_{critical}$), the pores are in the open state. When the pressure is released, the non-fouled pores return to their original liquid-filled state. The liquid-based gating mechanism allows selective, responsive, tunable and antifouling multiphase transport. Reprinted by permission from Macmillan Publishers Ltd: Nature, [142] copyright 2015.

Detergency effect. Schutzius et al. found that it was possible to obtain an underwater superoleophobic state regardless of the substrate material by introducing high-concentration surfactants (beyond CMC) into water (i.e. the detergency effect).[89] This effect might be used to decrease oil fouling on membranes during oil-water separation, with no requirement of surface micro-/nanotexturing or chemical modification of the membrane.[89] However, large amount of surfactants have to be present in the wastewater (for example, the CMCs for three typical surfactants, SDS, CTAB and Triton X-100 are 2566 mg/L, 328 mg/L and 155 mg/L, respectively,[69] which are comparable to the oil content in produced water (100-1000 mg/L)).[23] This limits

practical application of this method since surfactants are harmful to the aquatic ecosystem.[90]

6 Outlook

In addition to oil foulant, real-world oily wastewater contains various other kinds of foulants, such as organic foulants, inorganic foulants and biofilms.[18, 21, 50, 143] It is challenging to prevent fouling by these foulants at the same time. Property of the membrane (e.g., surface hydrophilicity and structure) and the wastewater (e.g., composition and concentration), configuration of the filtration module, and operation conditions are all relevant to membrane fouling during filtration. Except for the antifouling strategies introduced above, it is also helpful to apply pretreatment (e.g., flocculation, pre-filtering, etc.) to the oily wastewater before filtration, [38, 51, 111] or combine different treatment techniques to mitigate membrane fouling.[138, 139]

In the following we present the outlooks on the treatment of oily wastewater using membranes.

(1) Effective and reliable anti-fouling strategies still need to be explored, and some existing antifouling mechanisms need to be further clarified. For example, the combination of fouling-resistant and fouling-release mechanisms has been reported to be an effective antifouling strategy. However, its working principle and design criterion are far from known.

(2) Surfactant adsorption may alter membrane wettability towards water and oil, and thus degrades its antifouling property as well as efficiency in oil-water separation. As surfactants (or similar organic matters) are omnipresent in oily wastewater, it is highly important and also a big challenge to develop new strategies to eliminate the adverse effect of surfactant adsorption, or to develop novel membranes that can resist/reduce surfactant adsorption.

(3) Economic methods should be developed to prepare durable antifouling membranes. Although surfaces coated by zwitterionic polymers or cellulose nanofibrils have shown excellent antifouling property, the durability of such coatings and their large-scale fabrication method remain unsolved.

(4) Except for the surface chemistry, the surface geometry of the membrane also plays an important role in the antifouling property of the membrane.[144] Existing reports mostly studied the effect of pore size and surface roughness on the antifouling property (e.g. to enhance underwater oleophobicity), but it is not clear how specific geometrical structures (e.g. morphologies of pores) affect the oil-membrane adhesion as well as dynamic detachment of oil from the membrane surface. It is of great importance to identify the effect of specific membrane structure on the antifouling properties of membranes.

(5) In the experimental systems where surfactants and salts are involved, the underwater wetting properties of the membrane (e.g., oil contact angle under water) should be measured in water that contains the same amounts of surfactants and salts, since the surfactants and salts can influence the wetting behaviors significantly. Moreover, as the charges of membranes and oil droplets influence membrane fouling, the Zeta potentials of the membranes and oil droplets need to be characterized in order to specify the contribution of charges on fouling.[17, 24, 55, 112]

(6) Intelligent and responsive materials deserve more attention for developing antifouling membranes. For example, Ngang et al. fabricated PVDF/silica-poly(*N*-isopropylacrylamide) membranes which were thermo-responsive. It was found that by temperature swing the

irreversible fouling on the membrane could be reduced.[145] It is interesting to investigate whether such intelligent membranes that respond to different stimuli (e.g. photo-, electro-, and magneto-responsive membranes) could bring novel solutions for antifouling purpose.

(7) It is important to develop antifouling membranes that can survive under harsh conditions, such as wastewater with high salinity. For example, during treatment of highly saline wastewater, the hydrophilic coatings on the membrane surface may easily decompose.[72, 91] Inspired by seaweed, this problem can be solved by using alginate as the membrane or coating material.[72, 91] It is believed that similar bioinspired strategies will play important roles in treating oily wastewater using membranes under harsh conditions.

Acknowledgments

This work is supported by the “One Thousand Youth Talents” Program of China, and “One Hundred Talents” Program of Sun Yat-sen University. R.H.A.R. acknowledges the European Research Council for funding the Consolidator Grant SuperRepel (grant agreement no 725513).

References

- [1] Coday BD, Almaraz N, Cath TY. Forward osmosis desalination of oil and gas wastewater: Impacts of membrane selection and operating conditions on process performance. *Journal of Membrane Science*. 2015;488:40-55.
- [2] Zhang R, Shi W, Yu S, Wang W, Zhang Z, Zhang B, et al. Influence of salts, anion polyacrylamide and crude oil on nanofiltration membrane fouling during desalination process of polymer flooding produced water. *Desalination*. 2015;373:27-37.
- [3] Tummons EN, Tarabara VV, Chew JW, Fane AG. Behavior of oil droplets at the membrane surface during crossflow microfiltration of oil-water emulsions. *Journal of Membrane Science*. 2016;500:211-24.
- [4] Dickhout JM, Moreno Y, Biesheuvel PM, Boels L, Lanunertink RGH, de Vos WM. Produced water treatment by membranes: A review from a colloidal perspective. *Journal of Colloid and Interface Science*. 2017;487:523-34.
- [5] Feng L, Zhang ZY, Mai ZH, Ma YM, Liu BQ, Jiang L, et al. A super-hydrophobic and super-oleophilic coating mesh film for the separation of oil and water. *Angewandte Chemie International Edition*. 2004;43:2012-4.
- [6] Kota AK, Kwon G, Choi W, Mabry JM, Tuteja A. Hygro-responsive membranes for effective oil-water separation. *Nature Communications*. 2012;3:1025.
- [7] Shi Z, Zhang W, Zhang F, Liu X, Wang D, Jin J, et al. Ultrafast Separation of Emulsified Oil/Water Mixtures by Ultrathin Free-Standing Single-Walled Carbon Nanotube Network Films. *Advanced Materials*. 2013;25:2422-7.
- [8] Tummons EN, Chew JW, Fane AG, Tarabara VV. Ultrafiltration of saline oil-in-water emulsions stabilized by an anionic surfactant: Effect of surfactant concentration and divalent counterions. *Journal of Membrane Science*. 2017;537:384-95.
- [9] Chu Z, Feng Y, Seeger S. Oil/Water Separation with Selective Superantiwetting/Superwetting Surface Materials. *Angewandte Chemie International Edition*. 2015;54:2328-38.
- [10] Ma Q, Cheng H, Fane AG, Wang R, Zhang H. Recent Development of Advanced Materials with

- Special Wettability for Selective Oil/Water Separation. *Small*. 2016;12:2186-202.
- [11] Zhu X, Dudchenko A, Gu X, Jassby D. Surfactant-stabilized oil separation from water using ultrafiltration and nanofiltration. *Journal of Membrane Science*. 2017;529:159-69.
- [12] Wang B, Liang W, Guo Z, Liu W. Biomimetic super-lyophobic and super-lyophilic materials applied for oil/water separation: a new strategy beyond nature. *Chemical Society Reviews*. 2015;44:336-61.
- [13] Lu D, Zhang T, Ma J. Ceramic Membrane Fouling during Ultrafiltration of Oil/Water Emulsions: Roles Played by Stabilization Surfactants of Oil Droplets. *Environmental Science & Technology*. 2015;49:4235-44.
- [14] Kaner P, Rubakh E, Kim DH, Asatekin A. Zwitterion-containing polymer additives for fouling resistant ultrafiltration membranes. *Journal of Membrane Science*. 2017;533:141-59.
- [15] Kwon G, Post E, Tuteja A. Membranes with selective wettability for the separation of oil-water mixtures. *MRS Communications*. 2015;5:475-94.
- [16] Al-Anzi BS, Siang OC. Recent developments of carbon based nanomaterials and membranes for oily wastewater treatment. *RSC Advances*. 2017;7:20981-94.
- [17] Han G, de Wit JS, Chung T-S. Water reclamation from emulsified oily wastewater via effective forward osmosis hollow fiber membranes under the PRO mode. *Water Research*. 2015;81:54-63.
- [18] Mustafa G, Wyns K, Buekenhoudt A, Meynen V. Antifouling grafting of ceramic membranes validated in a variety of challenging wastewaters. *Water Research*. 2016;104:242-53.
- [19] Huang Y, Li H, Wang L, Qiao Y, Tang C, Jung C, et al. Ultrafiltration Membranes with Structure-Optimized Graphene-Oxide Coatings for Antifouling Oil/Water Separation. *Advanced Materials Interfaces*. 2015;2:1400433.
- [20] Moslehyani A, Ismail AF, Othman MHD, Matsuura T. Design and performance study of hybrid photocatalytic reactor-PVDF/MWCNT nanocomposite membrane system for treatment of petroleum refinery wastewater. *Desalination*. 2015;363:99-111.
- [21] Weschenfelder SE, Louvisse AMT, Borges CP, Meabe E, Izquierdo J, Campos JC. Evaluation of ceramic membranes for oilfield produced water treatment aiming reinjection in offshore units. *Journal of Petroleum Science and Engineering*. 2015;131:51-7.
- [22] Lu D, Zhang T, Gutierrez L, Ma J, Croue J-P. Influence of Surface Properties of Filtration-Layer Metal Oxide on Ceramic Membrane Fouling during Ultrafiltration of Oil/Water Emulsion. *Environmental Science & Technology*. 2016;50:4668-74.
- [23] Gohari RJ, Korminouri F, Lau WJ, Ismail AF, Matsuura T, Chowdhury MNK, et al. A novel super-hydrophilic PSf/HAO nanocomposite ultrafiltration membrane for efficient separation of oil/water emulsion. *Separation and Purification Technology*. 2015;150:13-20.
- [24] Zhang X, Tian J, Gao S, Zhang Z, Cui F, Tang CY. In situ surface modification of thin film composite forward osmosis membranes with sulfonated poly(arylene ether sulfone) for anti-fouling in emulsified oil/water separation. *Journal of Membrane Science*. 2017;527:26-34.
- [25] Li Y, Zhang ZZ, Ge B, Men XH, Xue QJ. A versatile and efficient approach to separate both surfactant-stabilized water-in-oil and oil-in-water emulsions. *Separation Purification Technology*. 2017;176:1-7.
- [26] Motin A, Tarabara VV, Benard A. Numerical investigation of the performance and hydrodynamics of a rotating tubular membrane used for liquid-liquid separation. *Journal of Membrane Science*. 2015;473:245-55.
- [27] Susan LY, Ismail S, Ooi BS, Mustapa H. Surface morphology of pvdf membrane and its fouling phenomenon by crude oil emulsion. *Journal of Water Process Engineering*. 2017;15:55-61.

- [28] Muppalla R, Jewrajka SK, Reddy AVR. Fouling resistant nanofiltration membranes for the separation of oil-water emulsion and micropollutants from water. *Separation and Purification Technology*. 2015;143:125-34.
- [29] Judd S, Jefferson B. *Membranes for Industrial Wastewater Recovery and Re-use*: Elsevier; 2003.
- [30] Zhu Y, Xie W, Li J, Xing T, Jin J. pH-Induced non-fouling membrane for effective separation of oil-in-water emulsion. *Journal of Membrane Science*. 2015;477:131-8.
- [31] Zhang F, Gao S, Zhu Y, Jin J. Alkaline-induced superhydrophilic/underwater superoleophobic polyacrylonitrile membranes with ultralow oil-adhesion for high-efficient oil/water separation. *Journal of Membrane Science*. 2016;513:67-73.
- [32] Zhu Y, Xie W, Zhang F, Xing T, Jin J. Superhydrophilic In-Situ-Cross-Linked Zwitterionic Polyelectrolyte/PVDF-Blend Membrane for Highly Efficient Oil/Water Emulsion Separation. *ACS Applied Materials & Interfaces*. 2017;9:9603-13.
- [33] Tian X, Jin H, Sainio J, Ras RHA, Ikkala O. Droplet and Fluid Gating by Biomimetic Janus Membranes. *Advanced Functional Materials*. 2014;24:6023-8.
- [34] Atadashi IM. Purification of crude biodiesel using dry washing and membrane technologies. *Alexandria Engineering Journal*. 2015;54:1265-72.
- [35] Kumar RV, Ghoshal AK, Pugazhenth G. Elaboration of novel tubular ceramic membrane from inexpensive raw materials by extrusion method and its performance in microfiltration of synthetic oily wastewater treatment. *Journal of Membrane Science*. 2015;490:92-102.
- [36] Obaid M, Barakat NAM, Fadali OA, Motlak M, Almajid AA, Khalil KA. Effective and reusable oil/water separation membranes based on modified polysulfone electrospun nanofiber mats. *Chemical Engineering Journal*. 2015;259:449-56.
- [37] Zhang E, Cheng Z, Lv T, Qian Y, Liu Y. Anti-corrosive hierarchical structured copper mesh film with superhydrophilicity and underwater low adhesive superoleophobicity for highly efficient oil-water separation. *Journal of Materials Chemistry A*. 2015;3:13411-7.
- [38] Agyemang FO, Li F, Momade FWY, Kim H. Effect of poly(ethylene oxide) and water on electrospun poly(vinylidene fluoride) nanofibers with enhanced mechanical properties as pre-filter for oil-in-water filtration. *Materials Chemistry and Physics*. 2016;182:208-18.
- [39] Dou Y, Tian D, Sun Z, Liu Q, Zhang N, Kim JH, et al. Fish Gill Inspired Crossflow for Efficient and Continuous Collection of Spilled Oil. *ACS Nano*. 2017:2477-85.
- [40] Wu J, Wei W, Zhao S, Sun M, Wang J. Fabrication of highly underwater oleophobic textiles through poly(vinyl alcohol) crosslinking for oil/water separation: the effect of surface wettability and textile type. *Journal of Materials Science*. 2017;52:1194-202.
- [41] Zhang J, Pan X, Xue Q, He D, Zhu L, Guo Q. Antifouling hydrolyzed polyacrylonitrile/graphene oxide membrane with spindle-knotted structure for highly effective separation of oil-water emulsion. *Journal of Membrane Science*. 2017;532:38-46.
- [42] Zhu Y, Chen D. Novel clay-based nanofibrous membranes for effective oil/water emulsion separation. *Ceramics International*. 2017;43:9465-71.
- [43] Du X, You S, Wang X, Wang Q, Lu J. Switchable and simultaneous oil/water separation induced by prewetting with a superamphiphilic self-cleaning mesh. *Chemical Engineering Journal*. 2017;313:398-403.
- [44] Li J-J, Zhou Y-N, Luo Z-H. Smart Fiber Membrane for pH-Induced Oil/Water Separation. *ACS Applied Materials & Interfaces*. 2015;7:19643-50.
- [45] Han Z, Li B, Mu Z, Niu S, Zhang J, Ren L. Energy-Efficient Oil-Water Separation of Biomimetic

- Copper Membrane with Multiscale Hierarchical Dendritic Structures. *Small*. 2017;13:1701121-n/a.
- [46] Shahkaramipour N, Tran TN, Ramanan S, Lin H. Membranes with Surface-Enhanced Antifouling Properties for Water Purification. *Membranes*. 2017;7:13.
- [47] Zhang Y, Cui M. Porous $\text{YxFeyZr}_{1-x}\text{YO}_2$ coated TiO_2 solid superacid particles/PVDF hybrid membranes with anti-fouling property. *Chemical Engineering Journal*. 2016;301:342-52.
- [48] Zhang Y, Wang L, Xu Y. ZrO_2 solid superacid porous shell/void/ TiO_2 core particles (ZVT)/polyvinylidene fluoride (PVDF) composite membranes with anti-fouling performance for sewage treatment. *Chemical Engineering Journal*. 2015;260:258-68.
- [49] Zhong Z, Xu F, Cao Y, Low Z-X, Zhang F, Xing W. Purifying condensed water with ceramic ultrafiltration membranes. *Journal of Chemical Technology and Biotechnology*. 2015;90:2092-9.
- [50] Zhang X, Guo Z, Zhang C, Luan J. Exploration and optimization of two-stage vacuum membrane distillation process for the treatment of saline wastewater produced by natural gas exploitation. *Desalination*. 2016;385:117-25.
- [51] Ochando-Pulido JM, Verardo V, Segura-Carretero A, Martinez-Ferez A. Technical optimization of an integrated UF/NF pilot plant for conjoint batch treatment of two-phase olives and olive oil washing wastewaters. *Desalination*. 2015;364:82-9.
- [52] Tang YP, Chan JX, Chung TS, Weber M, Staudt C, Maletzko C. Simultaneously covalent and ionic bridging towards antifouling of GO-imbedded nanocomposite hollow fiber membranes. *Journal of Materials Chemistry A*. 2015;3:10573-84.
- [53] Luo L, Han G, Chung T-S, Weber M, Staudt C, Maletzko C. Oil/water separation via ultrafiltration by novel triangle-shape tri-bore hollow fiber membranes from sulfonated polyphenylenesulfone. *Journal of Membrane Science*. 2015;476:162-70.
- [54] Liu D, Zhu J, Qiu M, He C. Antifouling performance of poly(lysine methacrylamide)-grafted PVDF microfiltration membrane for solute separation. *Separation and Purification Technology*. 2016;171:1-10.
- [55] Zhang G, Gao F, Zhang Q, Zhan X, Chen F. Enhanced oil-fouling resistance of poly(ether sulfone) membranes by incorporation of novel amphiphilic zwitterionic copolymers. *RSC Advances*. 2016;6:7532-43.
- [56] Shen X, Xie T, Wang J, Liu P, Wang F. An anti-fouling poly(vinylidene fluoride) hybrid membrane blended with functionalized ZrO_2 nanoparticles for efficient oil/water separation. *RSC Advances*. 2017;7:5262-71.
- [57] Li X, Ang WL, Liu Y, Chung T-S. Engineering design of outer-selective tribore hollow fiber membranes for forward osmosis and oil-water separation. *Aiche Journal*. 2015;61:4491-501.
- [58] Lu D, Cheng W, Zhang T, Lu X, Liu Q, Jiang J, et al. Hydrophilic Fe_2O_3 dynamic membrane mitigating fouling of support ceramic membrane in ultrafiltration of oil/water emulsion. *Separation and Purification Technology*. 2016;165:1-9.
- [59] Rajasekhar T, Trinadh M, Babu PV, Sainath AVS, Reddy AVR. Oil-water emulsion separation using ultrafiltration membranes based on novel blends of poly(vinylidene fluoride) and amphiphilic tri-block copolymer containing carboxylic acid functional group. *Journal of Membrane Science*. 2015;481:82-93.
- [60] Karimi E, Raisi A, Aroujalian A. TiO_2 -induced photo-cross-linked electrospun polyvinyl alcohol nanofibers microfiltration membranes. *Polymer*. 2016;99:642-53.
- [61] Qin D, Liu Z, Bai H, Sun DD, Song X. A new nano-engineered hierarchical membrane for concurrent removal of surfactant and oil from oil-in-water nanoemulsion. *Scientific Reports*. 2016;6:24365.

- [62] Mohammadi T, Kazemimoghadam M, Saadabadi M. Modeling of membrane fouling and flux decline in reverse osmosis during separation of oil in water emulsions. *Desalination*. 2003;157:369-75.
- [63] Field RW, Pearce GK. Critical, sustainable and threshold fluxes for membrane filtration with water industry applications. *Advances in Colloid and Interface Science*. 2011;164:38-44.
- [64] Hermia J. Constant pressure blocking filtration law application to powder-law non-Newtonian fluid. *Transactions of the Institution of Chemical Engineers*. 1982;60:183-7.
- [65] Salahi A, Mohammadi T, Behbahani RM, Hemati M. PES and PES/PAN Blend Ultrafiltration Hollow Fiber Membranes for Oily Wastewater Treatment: Preparation, Experimental Investigation, Fouling, and Modeling. *Advances in Polymer Technology*. 2015;34:21494.
- [66] Nazzal FF, Wiesner MR. Microfiltration of oil-in-water emulsions. *Water Environment Research*. 1996;68:1187-91.
- [67] Cumming IW, Holdich RG, Smith ID. The rejection of oil by microfiltration of a stabilised kerosene/water emulsion. *Journal of Membrane Science*. 2000;169:147-55.
- [68] Darvishzadeh T, Priezjev NV. Effects of crossflow velocity and transmembrane pressure on microfiltration of oil-in-water emulsions. *Journal of Membrane Science*. 2012;423:468-76.
- [69] Butt H-J, Graf K, Kappl M. *Physics and Chemistry of Interfaces*, 2nd ed.: Wiley-VCH, Berlin; 2006.
- [70] Grate JW, Dehoff KJ, Warner MG, Pittman JW, Wietsma TW, Zhang C, et al. Correlation of Oil–Water and Air–Water Contact Angles of Diverse Silanized Surfaces and Relationship to Fluid Interfacial Tensions. *Langmuir*. 2012;28:7182-8.
- [71] Tian X, Jokinen V, Li J, Sainio J, Ras RHA. Unusual Dual Superlyophobic Surfaces in Oil–Water Systems: The Design Principles. *Advanced Materials*. 2016;28:10652-8.
- [72] Cai Y, Lu Q, Guo X, Wang S, Qiao J, Jiang L. Salt-Tolerant Superoleophobicity on Alginate Gel Surfaces Inspired by Seaweed (*Saccharina japonica*). *Advanced Materials*. 2015;27:4162-8.
- [73] Liu N, Zhang M, Zhang W, Cao Y, Chen Y, Lin X, et al. Ultralight free-standing reduced graphene oxide membranes for oil-in-water emulsion separation. *Journal of Materials Chemistry A*. 2015;3:20113-7.
- [74] Yuan T, Meng J, Hao T, Wang Z, Zhang Y. A Scalable Method toward Superhydrophilic and Underwater Superoleophobic PVDF Membranes for Effective Oil/Water Emulsion Separation. *ACS Applied Materials & Interfaces*. 2015;7:14896-904.
- [75] Chang C-C, Kolewe KW, Li Y, Kosif I, Freeman BD, Carter KR, et al. Underwater Superoleophobic Surfaces Prepared from Polymer Zwitterion/Dopamine Composite Coatings. *Advanced Materials Interfaces*. 2016;3:1500521.
- [76] Xiong Z, Lin H, Zhong Y, Qin Y, Lia T, Liu F. Robust superhydrophilic polylactide (PLA) membranes with a TiO₂ nano-particle inlaid surface for oil/ water separation. *Journal of Materials Chemistry A*. 2017;5:6538-45.
- [77] Jayalakshmi A, Kim I-C, Kwon Y-N. Cellulose acetate graft-(glycidylmethacrylate-g-PEG) for modification of AMC ultrafiltration membranes to mitigate organic fouling. *RSC Advances*. 2015;5:48290-300.
- [78] Panda SR, Bhandaru N, Mukherjee R, De S. Ultrafiltration of oily waste water: Contribution of surface roughness in membrane properties and fouling characteristics of polyacrylonitrile membranes. *Canadian Journal of Chemical Engineering*. 2015;93:2031-42.
- [79] Fan L, Zhang Q, Yang Z, Zhang R, Liu Y-n, He M, et al. Improving Permeation and Antifouling Performance of Polyamide Nanofiltration Membranes through the Incorporation of Arginine. *ACS Applied Materials & Interfaces*. 2017;9:13577-86.

- [80] Yang X, He Y, Zeng G, Chen X, Shi H, Qing D, et al. Bio-inspired method for preparation of multiwall carbon nanotubes decorated superhydrophilic poly(vinylidene fluoride) membrane for oil/water emulsion separation. *Chemical Engineering Journal*. 2017;321:245-56.
- [81] Liu Y, Su Y, Cao J, Guan J, Zhang R, He M, et al. Antifouling, high-flux oil/water separation carbon nanotube membranes by polymer-mediated surface charging and hydrophilization. *Journal of Membrane Science*. 2017;542:254-63.
- [82] Shi C, Yan B, Xie L, Zhang L, Wang J, Takahara A, et al. Long-Range Hydrophilic Attraction between Water and Polyelectrolyte Surfaces in Oil. *Angewandte Chemie-International Edition*. 2016;55:15017-21.
- [83] Wang Z, Jin J, Hou D, Lin S. Tailoring surface charge and wetting property for robust oil-fouling mitigation in membrane distillation. *Journal of Membrane Science*. 2016;516:113-22.
- [84] Li L, Liu Z, Zhang Q, Meng C, Zhang T, Zhai J. Underwater superoleophobic porous membrane based on hierarchical TiO₂ nanotubes: multifunctional integration of oil-water separation, flow-through photocatalysis and self-cleaning. *Journal of Materials Chemistry A*. 2015;3:1279-86.
- [85] Wang Z, Lin S. Membrane fouling and wetting in membrane distillation and their mitigation by novel membranes with special wettability. *Water Research*. 2017;112:38-47.
- [86] Jin T, Song J, Zhu J, Nghiem LD, Zhao B, Li X-M, et al. The role of the surfactant sodium dodecyl sulfate to dynamically reduce mass transfer resistance of SPEEK coated membrane for oil-in-water emulsion treatment. *Journal of Membrane Science*. 2017;541:9-18.
- [87] Adamson AW, Gast AP. *Physical chemistry of surfaces*: Interscience publishers New York; 1967.
- [88] Kong J, Li K. Oil removal from oil-in-water emulsions using PVDF membranes. *Separation & Purification Technology*. 1999;16:83-93.
- [89] Schutzius TM, Walker C, Maitra T, Schonherr R, Stamatopoulos C, Jung S, et al. Detergency and Its Implications for Oil Emulsion Sieving and Separation. *Langmuir*. 2017;33:4250-9.
- [90] Sumisha A, Arthanareeswaran G, Thuyavan YL, Ismail AF, Chakraborty S. Treatment of laundry wastewater using polyethersulfone/polyvinylpyrrolidone ultrafiltration membranes. *Ecotoxicology and Environmental Safety*. 2015;121:174-9.
- [91] Li Y, Zhang H, Fan M, Zhuang J, Chen L. A robust salt-tolerant superoleophobic aerogel inspired by seaweed for efficient oil-water separation in marine environments. *Physical Chemistry Chemical Physics*. 2016;18:25394-400.
- [92] Padaki M, Murali RS, Abdullah MS, Misdan N, Moslehyani A, Kassim MA, et al. Membrane technology enhancement in oil-water separation. A review. *Desalination*. 2015;357:197-207.
- [93] Li C, Song C, Tao P, Sun M, Pan Z, Wang T, et al. Enhanced separation performance of coal-based carbon membranes coupled with an electric field for oily wastewater treatment. *Separation and Purification Technology*. 2016;168:47-56.
- [94] Lai GS, Yusob MHM, Lau WJ, Gohari RJ, Emadzadeh D, Ismail AF, et al. Novel mixed matrix membranes incorporated with dual-nanofillers for enhanced oil-water separation. *Separation and Purification Technology*. 2017;178:113-21.
- [95] Wang Z, Lin S. The impact of low-surface-energy functional groups on oil fouling resistance in membrane distillation. *Journal of Membrane Science*. 2017;527:68-77.
- [96] Wang Z, Hou D, Lin S. Composite Membrane with Underwater-Oleophobic Surface for Anti-Oil-Fouling Membrane Distillation. *Environmental Science & Technology*. 2016;50:3866-74.
- [97] Yin J, Zhou J. Novel polyethersulfone hybrid ultrafiltration membrane prepared with SiO₂-g-(PDMAEMA-co-PDMAPS) and its antifouling performances in oil-in-water emulsion application.

Desalination. 2015;365:46-56.

- [98] Kumar S, Mandal A, Guria C. Synthesis, characterization and performance studies of polysulfone and polysulfone/polymer-grafted bentonite based ultrafiltration membranes for the efficient separation of oil field oily wastewater. *Process Safety and Environmental Protection*. 2016;102:214-28.
- [99] Zhao X, Liu C. Enhancing the permeation and fouling resistance of PVDF microfiltration membranes by constructing an auto-soak surface. *RSC Advances*. 2016;6:113267-74.
- [100] Melbiah JSB, Nithya D, Mohan D. Surface modification of polyacrylonitrile ultrafiltration membranes using amphiphilic Pluronic F127/CaCO₃ nanoparticles for oil/water emulsion separation. *Colloids and Surfaces a-Physicochemical and Engineering Aspects*. 2017;516:147-60.
- [101] Zhao X, Su Y, Liu Y, Lip Y, Jiang Z. Free-Standing Graphene Oxide-Palygorskite Nanohybrid Membrane for Oil/Water Separation. *ACS Applied Materials & Interfaces*. 2016;8:8247-56.
- [102] Gao SJ, Sun JC, Liu PP, Zhang F, Zhang WB, Yuan SL, et al. A Robust Polyionized Hydrogel with an Unprecedented Underwater Anti-Crude-Oil-Adhesion Property. *Advanced Materials*. 2016;28:5307-14.
- [103] He K, Duan HR, Chen GY, Liu XK, Yang WS, Wang DY. Cleaning of Oil Fouling with Water Enabled by Zwitterionic Polyelectrolyte Coatings: Overcoming the Imperative Challenge of Oil-Water Separation Membranes. *ACS Nano*. 2015;9:9188-98.
- [104] Wu J, Lin W, Wang Z, Chen S, Chang Y. Investigation of the Hydration of Nonfouling Material Poly(sulfobetaine methacrylate) by Low-Field Nuclear Magnetic Resonance. *Langmuir*. 2012;28:7436-41.
- [105] Bengani P, Kou Y, Asatekin A. Zwitterionic copolymer self-assembly for fouling resistant, high flux membranes with size-based small molecule selectivity. *Journal of Membrane Science*. 2015;493:755-65.
- [106] Pal D, Neogi S, De S. Improved antifouling characteristics of acrylonitrile co-polymer membrane by low temperature pulsed ammonia plasma in the treatment of oil-water emulsion. *Vacuum*. 2016;131:293-304.
- [107] Qin D, Liu Z, Sun DD, Song X, Bai H. A new nanocomposite forward osmosis membrane custom-designed for treating shale gas wastewater. *Scientific Reports*. 2015;5:14530.
- [108] Xiang Y, Liu F, Xue L. Under seawater superoleophobic PVDF membrane inspired by polydopamine for efficient oil/seawater separation. *Journal of Membrane Science*. 2015;476:321-9.
- [109] Xue Q, Cao H, Meng F, Quan M, Gong Y-K. Cell membrane mimetic coating immobilized by mussel-inspired adhesion on commercial ultrafiltration membrane to enhance antifouling performance. *Journal of Membrane Science*. 2017;528:1-11.
- [110] Xue S, Li C, Li J, Zhu H, Guo Y. A catechol-based biomimetic strategy combined with surface mineralization to enhance hydrophilicity and anti-fouling property of PTFE flat membrane. *Journal of Membrane Science*. 2017;524:409-18.
- [111] Moghimifar V, Livari AE, Raisi A, Aroujalian A. Enhancing the antifouling property of polyethersulfone ultrafiltration membranes using NaX zeolite and titanium oxide nanoparticles. *RSC Advances*. 2015;5:55964-76.
- [112] Wang Y, Lin H, Xiong Z, Wu Z, Wang Y, Xiang L, et al. A silane-based interfacial crosslinking strategy to design PVDF membranes with versatile surface functions. *Journal of Membrane Science*. 2016;520:769-78.
- [113] Venkatesh K, Arthanareeswaran G, Bose AC. PVDF mixed matrix nano-filtration membranes integrated with 1D-PANI/TiO₂ NFs for oil-water emulsion separation. *RSC Advances*. 2016;6:18899-908.

- [114] He Y, Xu L, Feng X, Zhao Y, Chen L. Dopamine-induced nonionic polymer coatings for significantly enhancing separation and antifouling properties of polymer membranes: Codeposition versus sequential deposition. *Journal of Membrane Science*. 2017;539:421-31.
- [115] Xue Z, Wang S, Lin L, Chen L, Liu M, Feng L, et al. A Novel Superhydrophilic and Underwater Superoleophobic Hydrogel-Coated Mesh for Oil/Water Separation. *Advanced Materials*. 2011;23:4270-3.
- [116] Huang S, Wang D. A Simple Nanocellulose Coating for Self-Cleaning upon Water Action: Molecular Design of Stable Surface Hydrophilicity. *Angewandte Chemie International Edition*. 2017;56:9053-7.
- [117] Liu YW, Zhang CH, Wang ZQ, Fu X, Wei R. Scaly bionic structures constructed on a polyester fabric with anti-fouling and anti-bacterial properties for highly efficient oil-water separation. *RSC Advances*. 2016;6:87332-40.
- [118] Liu M, Wang S, Wei Z, Song Y, Jiang L. Bioinspired Design of a Superoleophobic and Low Adhesive Water/Solid Interface. *Advanced Materials*. 2009;21:665-9.
- [119] Zhang WB, Zhu YZ, Liu X, Wang D, Li JY, Jiang L, et al. Salt-Induced Fabrication of Superhydrophilic and Underwater Superoleophobic PAA-g-PVDF Membranes for Effective Separation of Oil-in-Water Emulsions. *Angewandte Chemie International Edition*. 2014;53:856-60.
- [120] Zhang W, Zhang F, Gao S, Zhu Y, Li J, Jin J. Micro/nano hierarchical poly(acrylic acid)-grafted-poly(vinylidene fluoride) layer coated foam membrane for temperature-controlled separation of heavy oil/water. *Separation and Purification Technology*. 2015;156:207-14.
- [121] Zeng G, He Y, Zhan Y, Zhang L, Shi H, Yu Z. Preparation of a Novel Poly(vinylidene fluoride) Ultrafiltration Membrane by Incorporation of 3-Aminopropyltriethoxysilane-Grafted Halloysite Nanotubes for Oil/Water Separation. *Industrial & Engineering Chemistry Research*. 2016;55:1760-7.
- [122] Liu Y, Wei R, Lin O, Zhang W, Du Y, Wang C, et al. Enhanced Hydrophilic and Antipollution Properties of PES Membrane by Anchoring SiO₂/HPAN Nanomaterial. *ACS Sustainable Chemistry & Engineering*. 2017;5:7812-23.
- [123] Kirschner AY, Chang C-C, Kasemset S, Emrick T, Freeman BD. Fouling-resistant ultrafiltration membranes prepared via co-deposition of dopamine/zwitterion composite coatings. *Journal of Membrane Science*. 2017;541:300-11.
- [124] Shao Q, He Y, White AD, Jiang S. Difference in Hydration between Carboxybetaine and Sulfobetaine. *The Journal of Physical Chemistry B*. 2010;114:16625-31.
- [125] Leng C, Han X, Shao Q, Zhu Y, Li Y, Jiang S, et al. In Situ Probing of the Surface Hydration of Zwitterionic Polymer Brushes: Structural and Environmental Effects. *The Journal of Physical Chemistry C*. 2014;118:15840-5.
- [126] Leng C, Hung H-C, Sieggreen OA, Li Y, Jiang S, Chen Z. Probing the Surface Hydration of Nonfouling Zwitterionic and Poly(ethylene glycol) Materials with Isotopic Dilution Spectroscopy. *The Journal of Physical Chemistry C*. 2015;119:8775-80.
- [127] Schlenoff JB. Zwitteration: Coating Surfaces with Zwitterionic Functionality to Reduce Nonspecific Adsorption. *Langmuir*. 2014;30:9625-36.
- [128] Zhu X, Loo H-E, Bai R. A novel membrane showing both hydrophilic and oleophobic surface properties and its non-fouling performances for potential water treatment applications. *Journal of Membrane Science*. 2013;436:47-56.
- [129] Zhang GF, Jiang JX, Zhang QH, Gao F, Zhan XL, Chen FQ. Ultralow Oil-Fouling Heterogeneous Poly(ether sulfone) Ultrafiltration Membrane via Blending with Novel Amphiphilic Fluorinated

Gradient Copolymers. *Langmuir*. 2016;32:1380-8.

[130] Zhang G, Jiang J, Zhang Q, Zhan X, Chen F. Amphiphilic poly(ether sulfone) membranes for oil/water separation: Effect of sequence structure of the modifier. *Aiche Journal*. 2017;63:739-50.

[131] Zhao X, Su Y, Dai H, Li Y, Zhang R, Jiang Z. Coordination-enabled synergistic surface segregation for fabrication of multi-defense mechanism membranes. *Journal of Materials Chemistry A*. 2015;3:3325-31.

[132] Zhao X, Su Y, Cao J, Li Y, Zhang R, Liu Y, et al. Fabrication of antifouling polymer-inorganic hybrid membranes through the synergy of biomimetic mineralization and nonsolvent induced phase separation. *Journal of Materials Chemistry A*. 2015;3:7287-95.

[133] Liu H, Raza A, Aili A, Lu J, AlGhaferi A, Zhang T. Sunlight-Sensitive Anti-Fouling Nanostructured TiO₂ coated Cu Meshes for Ultrafast Oily Water Treatment. *Scientific Reports*. 2016;6:25414.

[134] Zhang W, Lu X, Xin Z, Zhou C. A self-cleaning polybenzoxazine/TiO₂ surface with superhydrophobicity and superoleophilicity for oil/water separation. *Nanoscale*. 2015;7:19476-83.

[135] Li L, Liu L, Lei J, He J, Li N, Pan F. Intelligent sponge with reversibly tunable super-wettability: robust for effective oil-water separation as both the absorber and filter tolerate fouling and harsh environments. *Journal of Materials Chemistry A*. 2016;4:12334-40.

[136] Ye S, Cao Q, Wang Q, Wang T, Peng Q. A highly efficient, stable, durable, and recyclable filter fabricated by femtosecond laser drilling of a titanium foil for oil-water separation. *Scientific Reports*. 2016;6:37591.

[137] Huotari HM, Trägårdh G, Huisman IH. Crossflow Membrane Filtration Enhanced by an External DC Electric Field: A Review. *Chemical Engineering Research and Design*. 1999;77:461-8.

[138] Geng P, Chen G. Magnéli Ti₄O₇ modified ceramic membrane for electrically-assisted filtration with antifouling property. *Journal of Membrane Science*. 2016;498:302-14.

[139] Yang T, Qiao B, Li G-C, Yang Q-Y. Improving performance of dynamic membrane assisted by electrocoagulation for treatment of oily wastewater: Effect of electrolytic conditions. *Desalination*. 2015;363:134-43.

[140] Dudchenko AV, Rolf J, Shi L, Olivas L, Duan W, Jassby D. Coupling Underwater Superoleophobic Membranes with Magnetic Pickering Emulsions for Fouling-Free Separation of Crude Oil/Water Mixtures: An Experimental and Theoretical Study. *ACS Nano*. 2015;9:9930-41.

[141] Aveyard R, Binks BP, Clint JH. Emulsions stabilised solely by colloidal particles. *Advances in Colloid and Interface Science*. 2003;100:503-46.

[142] Hou X, Hu Y, Grinthal A, Khan M, Aizenberg J. Liquid-based gating mechanism with tunable multiphase selectivity and antifouling behaviour. *Nature*. 2015;519:70-3.

[143] Zhao Y, Zhang M, Wang Z. Underwater Superoleophobic Membrane with Enhanced Oil-Water Separation, Antimicrobial, and Antifouling Activities. *Advanced Materials Interfaces*. 2016;3:1500664.

[144] Brown PS, Bhushan B. Mechanically durable, superoleophobic coatings prepared by layer-by-layer technique for anti-smudge and oil-water separation. *Scientific Reports*. 2015;5:14030.

[145] Ngang HP, Ahmad AL, Low SC, Ooi BS. Preparation of thermoresponsive PVDF/SiO₂-PNIPAM mixed matrix membrane for saline oil emulsion separation and its cleaning efficiency. *Desalination*. 2017;408:1-12.