colloids and interfaces

Review

Special Wettable Membranes for Oil/Water Separations: A Brief Overview of Properties, Types, and Recent Progress

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Abstract: Periodical oil spills and massive production of industrial oil wastewater have impacted the aquatic environment and has put the sustainability of the ecosystem at risk. Oil–water separation has emerged as one of the hot areas of research due to its high environmental and societal significance. Special wettable membranes have received significant attention due to their outstanding selectivity, excellent separation efficiency, and high permeation flux. This review briefly discusses the fouling behavior of membranes and various basic wettability models. According to the special wettability, two major classes of membranes are discussed. One is superhydrophobic and superoleophilic; these membranes are selective for oil and reject water and are highly suitable for separating the water-in-oil emulsions. The second class of membranes is superhydrophilic and underwater superoleophobic; these membranes are highly selective for water, reject the oil, and are suitable for separating the oil-in-water emulsions. The properties and recent progress of the special wettable membranes are concisely discussed in each section. Finally, the review is closed with conclusive remarks and future directions.

Keywords: environment; water; interface; emulsions; superhydrophobic superhydrophilic

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1. Introduction

Water is the fundamental essence of life. The quality and sustainability of life on earth are only possible with a continuous water supply. The division of the water on the planet is amazing: 97.5% of water is present in the ocean, and, due to high salinity, unfit for daily purposes, and out of 2.5% of the freshwater, only 1% of water is accessible [1,2]. Rapid urbanization is enhancing water demands quickly. For instance, in cities, the global papulations increased from 0.8 billion to 4.4 billion from 1950 to 2020, reaching up to 6.7 billion, which would be 68.4% of the expected population in 2050 [3]. Thus, clean water access has become a critical challenge for the future. The severity of the situation can be assessed from the following statistics [4]:

I. More than 2 billion people live in water stress regions, and this is expected to increase dramatically in future;
II. 1 billion people are suffering to get safe and clean drinking water;
III. The usage of contaminated water is the reason for the death of 3.4 million people each year;
IV. Millions of people collecting water from a distance of at least 6 km.

The reclamation of the water may help in reducing the stress of water scarcity and also have a positive impact on the aquatic environment. Oil pollution is one of the leading causes of water contamination. There is no doubt that catastrophic effects on the marine environment have been observed after several reported periodical oil spill incidents [5]. Designing membranes with an excellent capacity to separate oil and water is highly significant [6–8]. Oil spills in water are not simple chemistry as it is a mixture of several components and a wide range of toxic ingredients. The oily wastewater from the industries conducts a range of aliphatic and aromatic organic compounds [9]. It severely impacts the food chain as the algae productivity is severely affected by the spilled oil, which ultimately negatively impacts the food chain. Adding oil-contaminated water or spilling oil in the water dangerously increases the organic matter in the water, and microorganisms consume excessive oxygen, which may prove fatal. The amount of dissolved oxygen may drop to a low level from the required concentration of 2 mg/L, which may cause lethal consequences for the aquatic environment [10]. Due to the deadly impact of the oily wastewater, the oil and water separation received significant importance [11,12]. Several traditional oil/water separation technologies, including electrochemical, filtration, flotation, gravity-based separation, centrifuge, and burning methods, are adopted to remove the oil from the water [13]. The burning of the oil may result in the formation of secondary environmental pollutants. Furthermore, the conventional methods are tedious, time-consuming, and may require manual operations [13,14]. Another major challenge associated with traditional methods is the incomplete separation of the oil/water mixtures. The oil may remain in the water, or the water may stay in the oil while separating the oil–water mixtures. Thus, more efficient methods are required for the oil/water mixture separations [15].

According to the droplet size, oily wastewater can be classified into immiscible and emulsified oil/water mixtures. The free oil/water mixture term is used when the diameter is greater than 150 μm, and the dispersion term is used when the diameter is in the range of the 20–150 μm, and the oil/water mixture is called emulsified when the diameter is less than 20 μm [16]. Separating the emulsified oil/water mixtures is a critical industrial and environmental challenge [17,18]. Conventional methods, including skimming and flotation, can remove the free and dispersed oil. In contrast, the oil that is stabilized with the help of surfactants cannot be removed by traditional gravity-based techniques due to the long settling time and surfactant stabilization. Thus, efforts have been made to treat the emulsified oil using demulsifiers to break the emulsions, and later, gravity-based separation is conducted. However, adding extra chemicals to treat the emulsified oil is considered environmentally unfriendly and expensive [19].

Recently, membranes have received significant attention in separation science [20–25]. Membranes are considered effective for separating oil/water mixtures due to their low energy cost, high separation efficiencies, satisfactory flux, and compact design [26–29]. Nano-structured polymer-based membranes are reported to treat oily wastewater [30]. The size exclusion principle is insufficient to form high-performance membranes for oil/water emulsions separations. More rigorous control of the surface chemistry is required when dealing with the oil/water separations. Recently, special wettable materials have been receiving significant attention for separating oil and water [31–33]. The special wettability and the controlled pore size can help to design membranes that provide high separation efficiency, excellent permeation flux, and low fouling tendency. The special wettable membranes are defined according to the characteristics of the surface and their response toward oil and water. Thus, the special wettable membranes can be superhydrophilic, superhydrophobic, superoleophilic, and superoleophobic, and these behaviors of the surfaces can be tuned by controlling the surface chemistry and its texture [34,35]. The membranes that are superhydrophilic and underwater superoleophobic selectively allow the water to pass and reject the oil [36]. These membranes are more effective for the separation of the oil-in-water emulsions. The membranes that surface behaves superhydrophobic and superoleophilic are preferred for separating the water-in-oil emulsion [37]. Several reviews have been written on special wettable materials and membranes for oil and water separations [38–44], and this field is continuously evolving [45–49]. This review briefly discusses the recent progress on membrane fouling, wettability models, and various types of special wettable membranes.

2. Fouling of the Membranes

It is well-known that the fouling of the membranes is one of the critical challenges [50–52]. The industries using the membrane-based process spend substantial time and economic resources cleaning these membranes. The fouling of the membranes can happen in several ways, such as (Figure 1) [53]:

(a) Complete pore blocking;
(b) Intermediate blocking;
(c) Standard blocking;
(d) Cake layer formation.

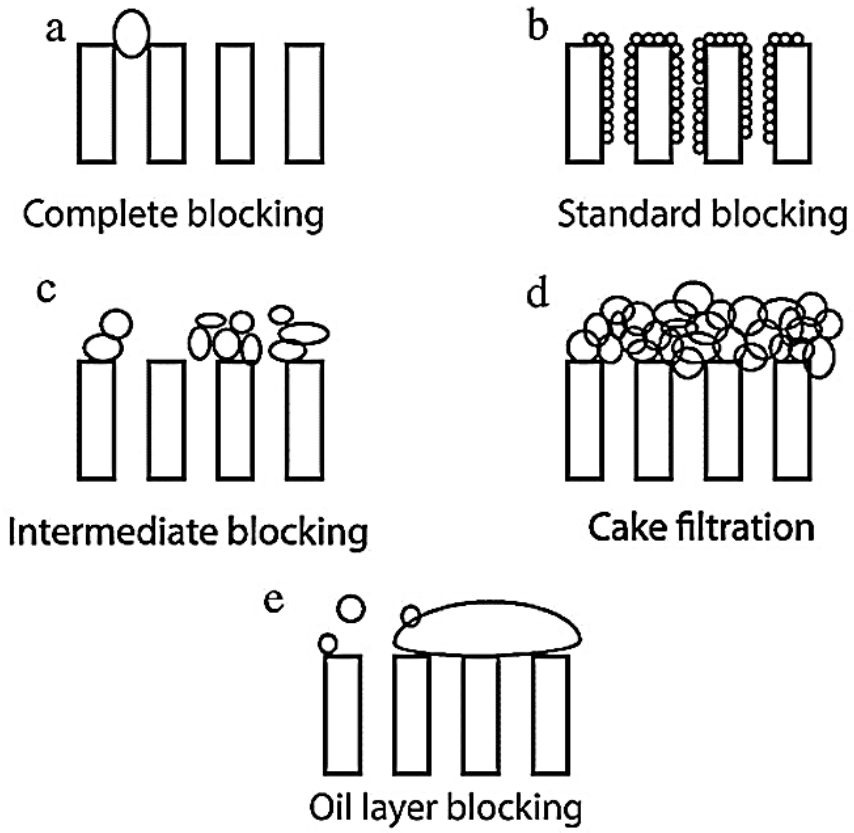

Figure 1. Schematic representation of the different fouling mechanisms taking place on the membrane surface [53]. Reprinted with permission from Ref. [53].

The bigger particles can completely block the pore, stopping the permeation through the membrane's pores. Complete pore blocking can also be called pore sealing. It is a general perception that in complete pore blocking, the particle settles and completely blocks the pore's opening without overlying other particles. The complete pore blocking reduced the number of channels for permeation [54], which significantly impacted the flux of the membrane. In intermediate blocking, the partial development of foulants on the pores' surface causes the pores' narrowing. The particles accumulate on the surface, and some may cause complete blocking in intermediate blocking, and it is also responsible for the flux decline.

The standard blocking causes the narrowing of the channels by adhering to the small-sized particles or droplets inside the pore. In other words, pore constriction has happened during the standard pore blocking. Due to the particles' deposition inside the membrane's pores, the overall pore volume is reduced. The pore volume decrease is directly related to the volume of the deposited particles inside the pore [55]. A uniform cake layer is formed on the entire membrane surface due to the accumulation and deposition of the particles, which are bigger in diameter than the membrane pore size. The cake layer is usually formed when the pores are already blocked with the initial stage of fouling, or the membrane is dense, and no pore is available for blocking. In cake filtration, a secondary membrane layer is formed on the membrane surface due to the accumulation of multiple layers of particles. The cake filtration may enhance the concentration polarization, which affects the rejection efficiency of the membranes and significantly decreases the membrane flux due to the hydraulic resistance created by the cake layer [54,56]. The cake fouling is not impermeable and can be reversed with suitable treatment, such as backwashing and flushing [57].

In several studies, during the separation of the oil/water emulsions, the fouling has been mentioned with the above one or two mechanisms; however, the fouling that happened during the liquid–liquid separation is not simple and sometimes tough to define with the above mechanisms. Emulsified liquid droplets are different from solid particles. The oil droplet or emulsified liquid size and shape depends upon several factors, including the shear rate, interfacial tensions, and composition of the liquid phases. The oil droplet or other liquid droplets can deform, break, or coalescence Thus, oil fouling differs from solid particle fouling as the emulsions are liquid droplets that can easily diffuse to form a continuous compact layer near the membrane, which is sometimes tough to remove with simple cleaning methods. A more in-depth understanding of liquid fouling is required to deal with membrane fouling during oil/water separation.

Thus, chemical cleaning is recommended to restore the membrane's flux. Cleaning of the membranes is usually proposed according to the type of membrane. The membranes used for the oil and water separation can be ceramic [58] or polymeric [59]. The various chemicals have been applied, which include the SDS, Na_2CO_3, HCl, H_2SO_4, EDTA, NaOH, HNO_3, H_3PO_5, and their combinations for the cleaning of the membranes. It has been found that the combination of the SDS and the EDTA found effective in cleaning the fouled membrane [60]. With suitable modification, the effectiveness of the cleaning agent can be improved for certain oil/water separation membranes [61]. The membranes developed with special wettability can offer better anti-fouling characteristics [62]. Therefore, better engineering and more control of the surface chemistry are required to produce high-performing anti-fouling membranes.

3. Contact Angle and Wettability Models

All materials have a particular wettability pattern according to their intrinsic surface behavior [63,64]. The material's wettability depends upon the chemical composition and the surface morphology of the materials [65]. The wettability of the surfaces is usually controlled by introducing surface roughness [66] and certain functionalities, which produce special wettable surfaces that are responsive to certain liquids [67]. The contact angle is one of the critical parameters to measure the wettability of the solid surface quantitively [68] due to its simplicity and ease in apprehending the wettability by the contact angle measurement while evaluating the affinity between the liquids and the solid surfaces [69] The wetting behavior of the surfaces or materials can be categorized into four types [70]:

(a) Hydrophilic: The water contact angle should be in the range of $10° < \theta < 90°$;
(b) Hydrophobic: The water contact angle should be in the range of $90° < \theta < 150°$;
(c) Superhydrophilic: The water contact angle should be in the range of $0° < \theta < 10°$;
(d) Superhydrophobic: The water contact angle should be in the range of $150° < \theta < 180°$.

Various theories or definitions of the contact angle keep evolving with time (Figure 2). The mathematical equations keep moving to the next stage with more insight into the special wettable surfaces. Thomas Young has given the contact angle quantitative expression for smooth and flat surfaces [71].

$$cos\theta = (\gamma SV - \gamma SL)/\gamma LV \quad (1)$$

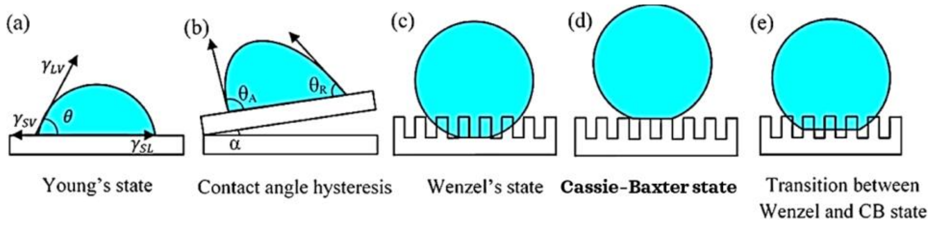

Figure 2. Various states of a water droplet on a solid surface [70]. Reprinted with permission from Ref. [70]. Copyright 2020 American Chemical Society.

In Equation (1), the γSV, γSL, and γLV represent the interfacial tension between solid–vapor, solid–liquid, and liquid–vapor. Young equation revealed the contact angle for the smooth surfaces. However, surfaces are usually not smooth and may have some roughness. There was a need to develop the contact angle model on rough surfaces. A Wenzel model was introduced by Robert N. Wenzel [72] for rough surfaces, and it was assumed that the liquid under the observation of contact angle is wholly entered into the grooves of the rough substrate. The water drop is pinned on the surface and unable to roll on the surface. The following equation measures the contact angle in the Wenzel model.

$$cos\theta \mathrm{w} = \mathrm{r}cos\theta \quad (2)$$

In Equation (2), the θ and θw represent the Young and the Wenzel contact angle. The "r" represents the roughness factor. From the Wenzel model, the liquid should penetrate the grooves of the solid surfaces, but this model cannot fit those rough surfaces where the liquid does not enter the grooves of the rough surfaces. For chemically inhomogeneous surfaces, the Cassie–Baxter model was proposed and shown in Equation (3).

$$cos\theta \mathrm{CB} = f1cos\theta 1 + f2cos\theta = f(cos\theta + 1) - 1 \quad (3)$$

In Equation (3), the θCB represents the Cassie–Baxter contact angle, and f indicates the liquid–solid contact surface area fraction. As in the case of the Cassie–Baxter contact angle, the air is trapped between the liquid and solid substrate as the surface is inhomogeneous. Due to this, the water drop rolls easily as it is not pinned or entered into the groove of the surface and contact angle hysteresis is usually small in this case.

4. Brief Discussion of Polymers Used in Oil/Water Separation

Polysulfone (PS) and its derivatives are among the most important and commonly utilized membrane materials [73–76]. This is because they are chemically, thermally, and oxidatively stable and have high mechanical strength. The properties of polysulfone or polyethersulfone membranes can be tuned using different additive materials [77]. Traditional PS membranes are synthesized via the phase inversion process. As a solvent, PS can be mixed with different common solvents, including DMF, DMAA, DMSO, formylpiperidine morpholine, and N-methylpyrrolidone (NMP) [78], and some green solvents, such as Rhodiasolv PolarClean, can also be used [79]. Due to hydrophobicity, these membranes are fouled quickly while separating the oil-in-water emulsion separation. Hydrophilic organic or inorganic materials are incorporated through several routes to make them suitable for oil/water separation applications. Hydrophilic polymers can be mixed into the casting solutions to prepare the mixed matrix membrane for oil/water separation applications. Bentonite, a hydroaluminosilicate that aggressively absorbs water, is used to increase membrane hydrophilicity [80]. Similarly, the hydrophilic magnesium dihydroxide particles mixing with the polyether sulfone hollow fiber membranes have lowered the water contact angle from 69.5° to 16.4°. The permeability of the produced hydrophilic membranes was increased from 39 to 573 LMH, and oil retention nearly approached 100%. Electron microscopy confirmed membrane morphological alterations [81]. Sulphonated Carbon

Soot-Polysulphone Membranes separated diesel-in-water emulsions with a separation efficiency of 99.9%, water flux of 314 LMH, and exhibited an excellent flux recovery of 92% [82].

PVDF is another polymer that has been extensively explored for oil–water separation applications. PVDF is a semi-crystalline polymer having the repeating unit of $(CH_2\text{-}CF_2)n$ and possesses good mechanical, chemical, and thermal stability [83]. Similar to PS, the PVDF is also facing the problem of rapid fouling during the treatment of the oil-in-water emulsions due to its hydrophobic nature. The hydrophilicity and anti-fouling behavior of the PVDF membranes can be improved using physical and chemical methods [84]. Sometimes, the coating enhances the membranes' anti-fouling behavior but decreases the membranes' flux due to adding the extra barrier layer. Therefore, during the modification process, it is essential to use such strategies which reduce the additional permeation resistance, and it can be controlled by decreasing the coating layer thickness, developing new hydrophilic materials with inherently high-water permeability, and avoiding the blocking of membrane pores to maintain the membrane efficiency [85]. Blending the PVDF with the amphiphilic hyperbranched-star polymer improved the protein resistance and the hydrophilicity of the membranes [86]. It has been that membranes coated with titanium dioxide (TiO_2) are very permeable and fouling-resistant [87]. Similarly, Tannic acid-graphene oxide (TA-GO) and titanium dioxide (TiO_2) were co-deposited on an electrospun PVDF membrane as part of a surface modification process based on metal polyphenol coordination. To prevent membrane compacting, TiO_2 was injected between GO layers. TA and Fe^{3+} enhance interlayer force via covalent, cation, and coordination bonds. The designed membrane has shown a strong flux of 243.11 LMH and excellent oil rejection of greater than 98%) [88]. By molecular grafting with three amino silanes, researchers construct superamphiphilic and superoleophobic PVDF membranes. Due to chemistry, nanostructuring, and roughness, molecular grafting gave new characteristics. After grafting, membranes showed dry and wet in-air superamphiphilicity. In water, the membrane is superoleophobic and repels oil droplets. Under oil, the membrane displayed superhydrophobicity but still permitted water droplet attachment. After construction, modification, and physicochemical characterization, membranes were evaluated for oil/water separation. The functionalized membranes rejected >99% oil and recovered flux. These results indicate the potential for molecular membrane grafting for separation and purification [89]. The properties of the PVDF can be tuned for desired applications using a range of polymeric aninorganicic materials, including amino silanes [89], alkylamines [90], and titanium oxide [91], hydrophilic layers, dopamine [92], cellulose [93], and another polymer mixing [94].

Apart from the PS, PES, and PVDF, other polymers, such as PAN, PVA, polyether ether ketone, and polybenzimidazole, were also used for the oil and water separation. Only those polymeric membranes are considered effective for industrial applications with long shelf life and anti-fouling. These membranes can be used for a longer time for industrial applications. For instance, PEEK has excellent potential to develop solvent resistance membranes. The combination of the PANI/PEEK significantly improved the pure water permeation flux to 302.5 LMH under optimal testing circumstances; PANI/PEEK membrane exhibited excellent anti-fouling behavior and flux recovery rate [95]. From this discussion, it can be concluded that a range of polymeric and ceramic materials are available to explore for oil/water separation applications.

5. Types of Special Wettable Membranes

The solid particles are usually separated on the principle of the size exclusion principle as the solid particles have well-defined boundaries. However, the separation of the oil–water emulsions is entirely different compared to the solid particles. Under pressure, tiny droplets can be squeezed in the dispersed phase and deformed, which may make them able to pass through pores that are smaller than their sizes [96,97]. It is indicated that making the tight membrane and high operating pressure may not solve the challenge of low separation efficiencies. Therefore, the special wettable surfaces are receiving significant attention along with the controlled pore size to deal with the oil/water mixtures and emulsions [98]. Based on the special wettability, these materials can be grouped into two major groups (Figure 3):

(a) Superhydrophobic and superoleophilic materials;
(b) Superhydrophilic and underwater superoleophobic materials.

The concept and details of these materials and membranes are briefly discussed in the following subsections [99].

Figure 3. Design of the superwetting porous materials and the mechanism of oil/water separation or emulsion separation [100]. Reprinted with permission from Ref. [100] Copyright © 2023 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

5.1. Superhydrophobic and Superoleophilic Membranes

The long-lasting superhydrophobic surfaces have received significant attention due to their high demands in the range of applications [99,101,102]. The superhydrophobic coating/surfaces have high needs in waterproof clothing, anti-icing, self-cleaning, transparency, gas permeability, anti-corrosion, drag reduction, fog harvesting, stain resistance, and oil/water separation applications [103–105] (Figure 4). Super-hydrophobic membranes and materials are receiving unprecedented attention for oil–water separation [106,107]. Superhydrophobic membranes are famous for water-in-oil emulsions compared to oil-in-water emulsions [108]. The superhydrophobic membranes also remove the water from the lubricating oil [109].

In some reports, it has been mentioned that the hydrophobic surface is not sufficient to prevent the water from passing. With just a hydrophobic surface, both water and oil can pass [110]. In the case of the water-in-oil emulsion, the water is the dispersed phase, and the oil is the continuous phase. Thus, such membranes are favorable, which selectively allow the passage of the oil and reject the water. Therefore, the superhydrophobic surfaces have a strong affinity for the oil and demonstrate a solid repellence to water.

Furthermore, the anti-fouling behavior of the membranes significantly increases as the low surface energy surface intrinsically rejects the water and is not allowed to settle down on the surface while separating the water-in-oil emulsions [111]. As discussed, designing the superhydrophobic surfaces requires some basic surface roughness requirements and controlling the membrane surface's chemical composition to produce a low-energy surface. The combination of both result in a superhydrophobic surface that strongly repel the water and allow the oil to spread and penetrate the membranes quickly. The roughness can be produced by several means, including electrochemical methods, chemical etching, physical deposition, spraying, or growth of nanoparticles on the surface [112,113]. In Figure 5, the mesh functionalization procedure is explained to produce low surface energy on the surface of the mesh. In general, first, the activation and reactive groups are generated on the surface of the mesh, which can help produce the necessary roughness on the surface. Then, the surface is linked with the long-chain alkyl groups to lower the surface energy. In Figure 5A, the water drop behavior before functionalization is shown where the water drop has a strong affinity for water. After functionalizing the surface, it becomes superhydrophobic and strongly repels the water (Figure 5B) [114]. The rational functionalization of the surfaces even can convert the super-hydrophilic surfaces to superhydrophobic ones and become effective for the selective separation of oil from the water [103]. For instance, a composite membrane consisting of microcrystalline cellulose and PVDF was prepared by directly mixing. Then, functionalization with the lauric acid by grafting method has shown the water contact angle of 153° ± 2° with a separation efficiency greater than 99% [115].

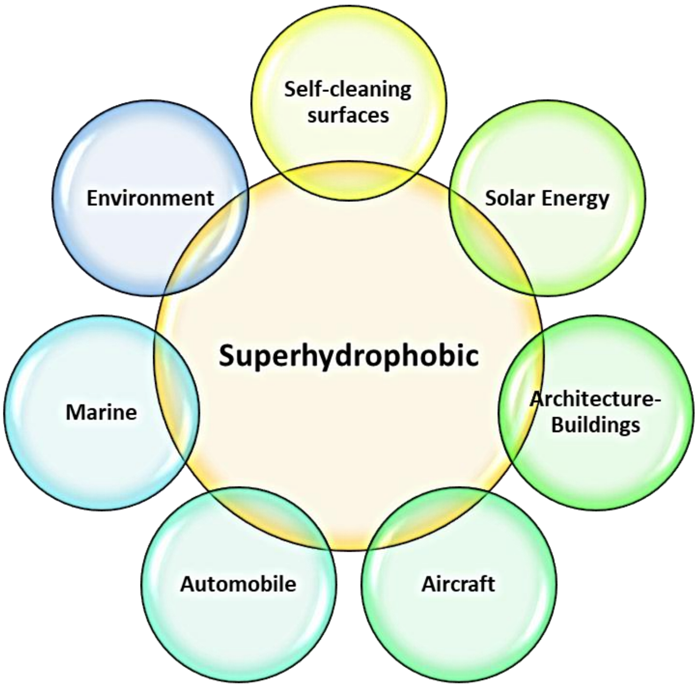

Figure 4. Applications of superhydrophobic surfaces.

Zhanjian Liu [116] reported the electrospun membranes with a water contact angle of 171° and achieved an excellent tensile strength of 5.225 MPa. Similarly, the electrospun polyimide (PI) nanofibrous membrane is prepared, rough surfaces are produced with the help of the tannic acid metal complex, and superhydrophobicity is achieved by modification with the PDMS. The designed superhydrophobic electrospun membrane has shown a high flux of 6935 LMH with a high separation efficiency of 99%. It also possesses additional UV shielding and self-cleaning characteristics, making it appropriate for oil/water separation [117]. Deke Li [118] has developed a superhydrophobic membrane using the PDMS for oil/water show, which also shows the flame Retardancy behavior.

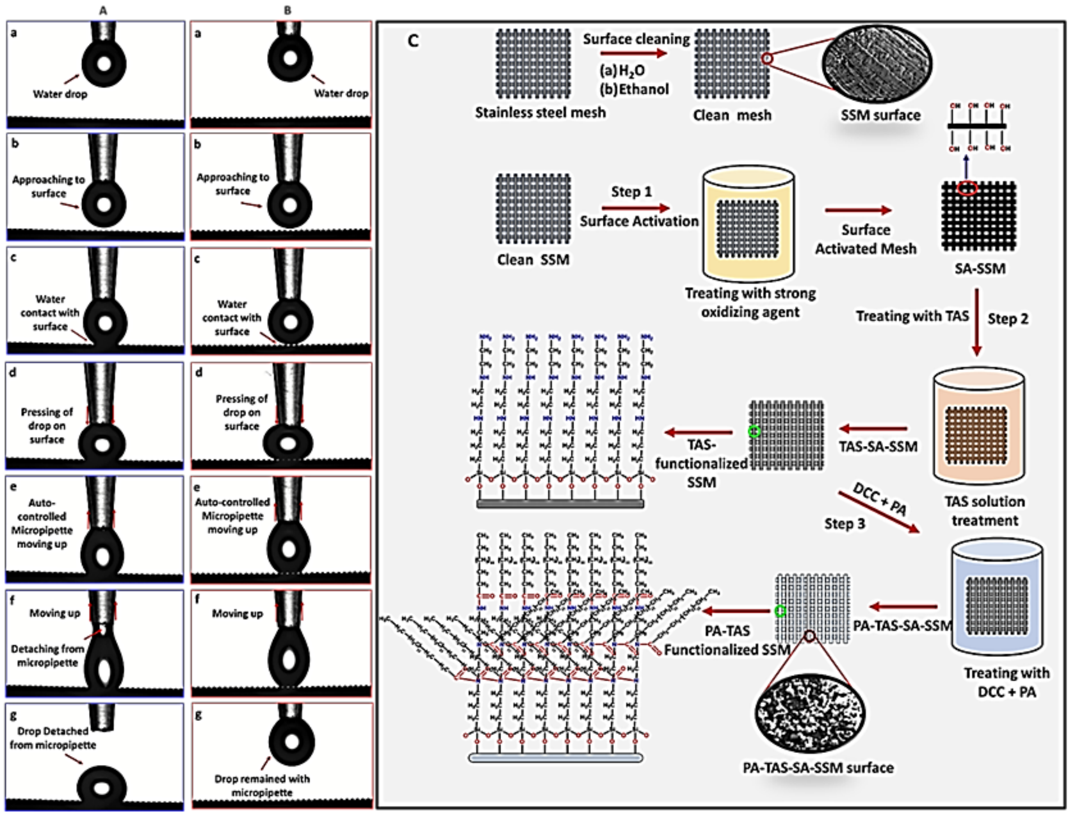

Figure 5. Response of water drop controlled by auto-controlled micropipette on the surface of the (**A**) SSM and (**B**) PA-TAS-SA-SSM. (**a**) Waterdrop produced by the micropipette, (**b**) Waterdrop approaching the surface, (**c**) Waterdrop contact with the surface, (**d**) Drop pressing on the surface, (**e**) Auto controlled micropipette moving up, (**f**) Continuation of upward movement, and (**g**) Auto-controlled micropipette pulled over. (**C**) Schematic stepwise illustration of the fabrication of the PA-TAS-SA-SSM [114]. Reprinted with permission from Ref. [114]. Copyright 2021 Elsevier Ltd. All rights reserved.

Apart from designing the superhydrophobic and superoleophilic membranes, there is a need to develop such membranes which can withstand harsh acidic and basic conditions. Tingting Fan et al. [119] prepared superhydrophobic-superoleophilic polyphenylene sulfide membrane, which can stand in extreme conditions, has also shown excellent rejection of water greater than 99.9% (Figure 6). The surface topography and the surface chemistry can also be controlled with the help of 3D printing. Three-dimensional printing was used to develop the superhydrophobic micro-/nanoporous membranes using fluoropolymer ink. The fluoropolymer enhanced the tendency of the membranes to stand with the abrasions. By changing the porogen ratio, the pore size of the membranes can be tuned from 30 to 300 nm [120].

Gravity-driven superhydrophobic membranes are also receiving significant attention due to their cost-effectiveness and ease of operation. The gravity-driven behavior is only possible when the surface possesses special wettability. Yi-Ting Tsai et al. [121] have designed the electrospun nanofibrous membranes using the blend poly(methyl methacrylate)/polydimethylsiloxane. The designed membranes have shown the excellent capability to separate and breakdown the various emulsions, such as water-in-hexane, water-in-hexadecane, water-in-diesel, and water-in-soybean, under gravity with incredible separation efficiencies of 99.0%, 99.5%, 99.25%, and 97.75%, respectively. It has been found that the methyl group presence rejects the water and prevents them from passing through the membrane, which results in the breakdown of several complex oils (Figure 7).

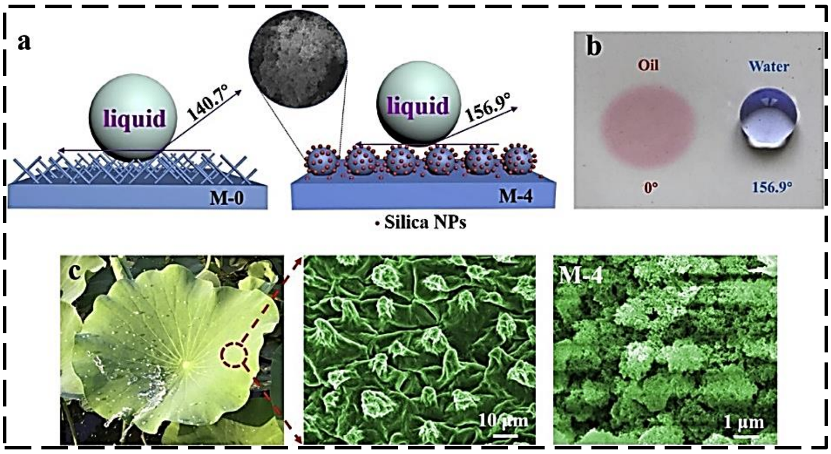

Figure 6. (**a**) Diagrams illustrate the effect of bottom surface structure of M-0 and M-4 on the hydrophobic; (**b**) Photograph of pure water and oil droplets on the M-4 bottom surface; (**c**) Optical photograph and SEM image of lotus leaf [119]. Reprinted with permission from Ref. [119]. Copyright 2019 Elsevier B.V. All rights reserved.

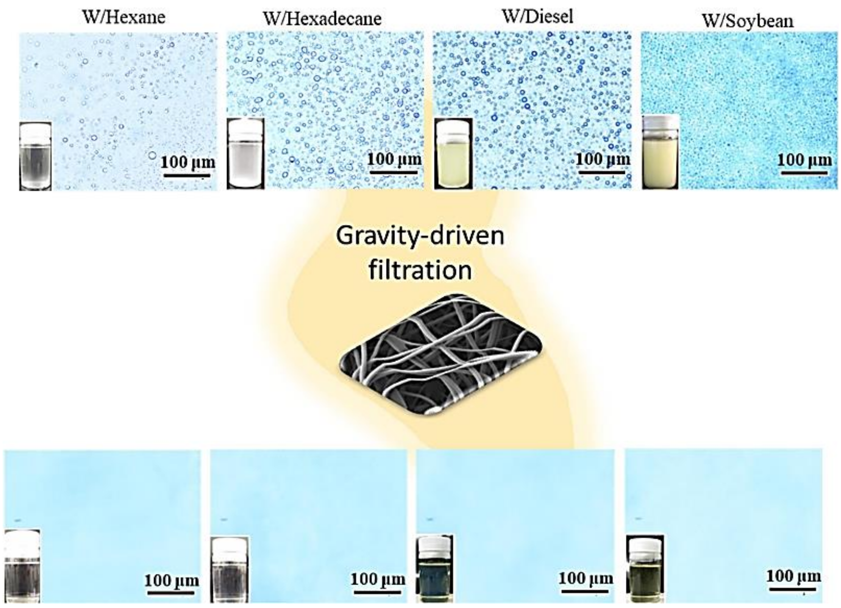

Figure 7. Optical micrographs of the feed emulsions (**top part**) and permeates (**bottom part**) using PMMA/60PDMS nanofibrous membrane under the sole influence of gravity [121]. Reprinted with permission from Ref. [121]. Copyright © 2023 Elsevier B.V. All rights reserved.

Several membranes have been reported to separate the layered oil/water mixtures. Ying Su et al. [122] reported the superhydrophobic and superlipophilic nanofiber membrane that was decorated with a pine needle-like structure. The pine needle-like structure was grown with the help of the TiO_2 nanorods using the hydrothermal method. This sort of structure results in increasing the surface roughness of the membranes, and, later on, the superhydrophobicity and super-lipophilicity were achieved using fluorination treatment. The fluorination treatment produced the membrane with an oil contact angle of 0° and a water contact angle of 155.0° (Figure 8). The separation efficiency was greater than 99%. The comparison of the various superhydrophobic membranes for oil/water separation can be seen in Table 1.

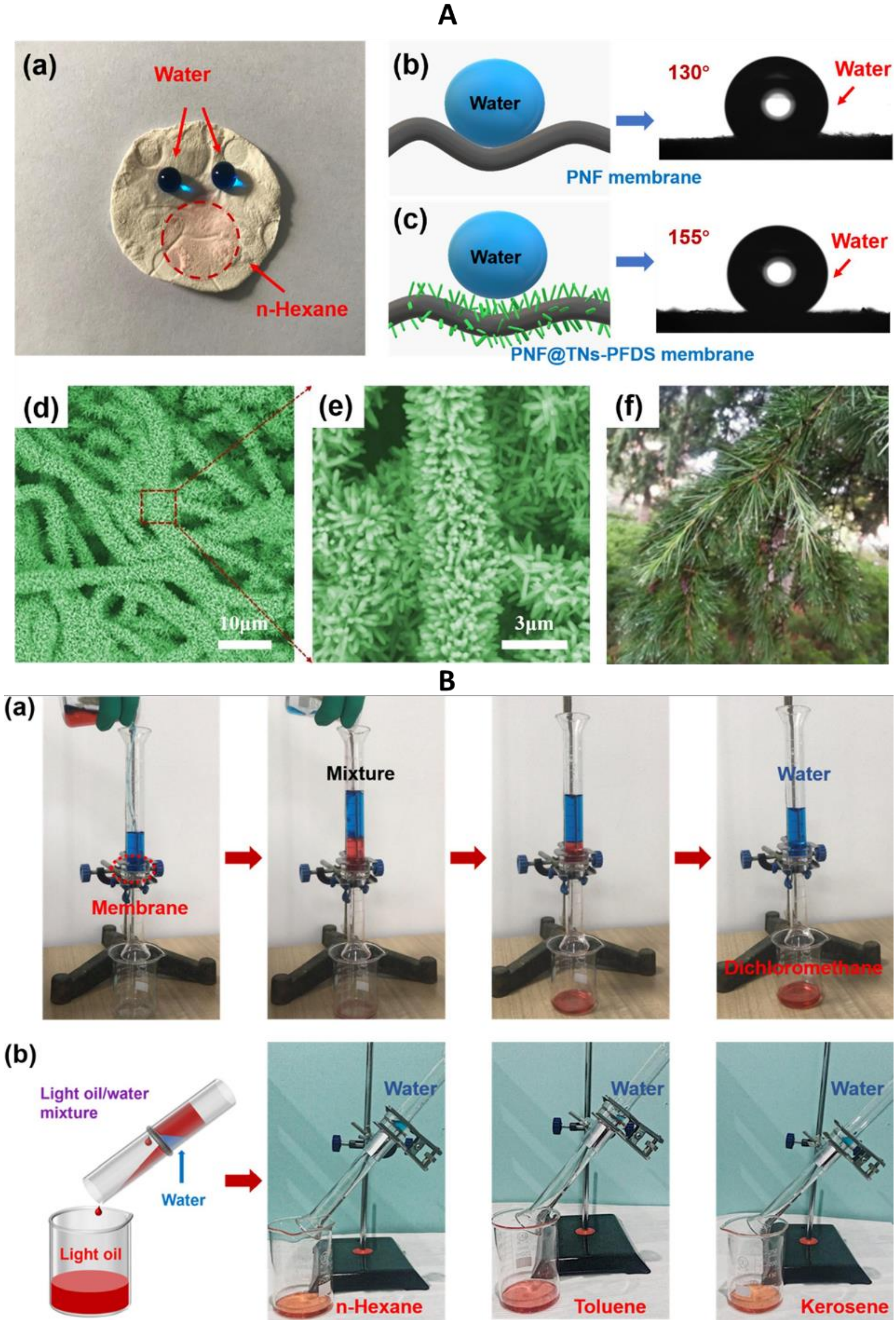

Figure 8. (**A**) (**a**) The state of water droplets and oil droplets (n-hexane) on the surface of the PNF@TNs-PFDS, the water, and the oil droplets were dyed to blue and red, respectively; (**b**) The WCA of PNF membrane; (**c**) PNF@TNs-PFDS fiber membrane; (**d**,**e**) SEM images of robust pine needle-like TNs; and (**f**) Photograph of pine needle. (**B**) Oil/water separation process of (**a**) heavy oil and (**b**) light oil [122]. Reprinted with permission from Ref. [122].

Table 1. Comparison of the performance of the Superhydrophobic membranes for oil/water separation.

Membranes	Filtration Type	Emulsion (Water-In-Oil or Oil/Water Mixtures	Pressure (Bar)	Water Contact Angle	Flux ($Lm^{-2}h^{-1}$)	Separation Efficiency	Ref.
Superhydrophobic isotactic polypropylene microporous membranes	Microfiltration	Oil Used: n-hexane, chloroform, and kerosene	0.9	153°	1230 ± 42	-	[111]
PDMS/TA-Mn+/PI nanofibrous membrane	Microfiltration	Oil Used: dichloromethane, chloroform, 1,2-dichloroethane, bromobenzene, and tetrachloromethane	Gravity	153.64 ± 1.6°	6935	99%	[117]
PMMA/60PDMS nanofibrous membrane	Microfiltration	Oil Used: Hexane hexadecane Diesel, and Soybean	Gravity	154°		99.5%	[121]
PML membrane	Microfiltration	Oil Used: Xylene, kerosene	Gravity	153° ± 2°	130–8800	99%	[115]
poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) nanofiber (PNF) membranes	Microfiltration	Oil Used: Dichloromethane, n-hexane, kerosene and toluene	Gravity	155.0°	9845	99.99%	[122]
Nano-structured ZnO/CuO mesh membrane	Microfiltration	Oil Used: Chloroform and n-hexane	Gravity	161.2° ± 1.5°	above 2000	>99.9%	[123]
BN-CuSA2 membrane	Microfiltration	Oil Used: dichloromethane kerosene	Gravity	162.3°	1667.63	>95%	[124]
CNTs Reinforced Porous Electrospun Superhydrophobic Membrane	Microfiltration	Oil Used: dichloromethane, chloroform, 1,2-dichloroethane,	Gravity	152°	9270	>99%	[125]
Carbon fiber membrane	Microfiltration	Oil Used: Dichloromethane, petroleum ether, ethyl acetate, carbon tetrachloride, toluene	Gravity	155.9°	3590	98%	[126]
polyurethane acrylate -based superhydrophobic membranes		Oil Used: Hexane	0.02	-	-	∼97%	[127]

One of the critical challenges associated with superhydrophobic and superoleophilic membranes is limited recyclability [128]. The membranes may lose their special wettability after some cycles, affecting their separation performances. Therefore, more robust and technically stable superhydrophobic and super-oleophilic membranes are required, which can sustain for a longer time and do not lose their special wettability after multiple cycles. Researchers have recently been trying to develop inorganic and organic hybrid special wettable membranes that demonstrate better chemical stability while separating the oil/water mixtures. Fluorine-based linkers or organic moieties are frequently used to produce superhydrophobic and super-oleophilic surfaces, and fluoro moieties or polymers are considered a serious environmental hazard. The fluoro modification is expensive and may also release highly toxic and perfluoroalkyl sulfonates or carboxylates into the ecosystem [129]. It is highly undesired that the fixation on one environmental or industrial problem introduces a second one. The fluorine-free systems are highly desired for oil/water separation applications. However, there are several examples in which fluorine-free methods have been used for oil/water separation [123,130–132]. More significant efforts are required in this direction to introduce more robust and environmentally friendly surfaces to treat the oil/water mixtures.

5.2. *Superhydrophilic and Underwater Superoleophobic Membranes*

Industrial processes, such as petroleum refining, petrochemical manufacturing, and metal finishing, all generate wastewater consisting of oil-in-water (O/W) emulsions daily. Disposal of oily wastewater presents environmental and financial challenges; hence materials and procedures that efficiently separate oil from water are required. The membranes-based technologies are becoming famous for treating oily wastewater [133]. Membrane function is severely diminished when oil and surfactants adsorb onto the membrane surface and/or into the membrane pores. Recently, oil removal from water using hydrophobic and oleophilic materials have attracted much attention [134,135]. It has been thoroughly covered in the previous section. However, the superhydrophobic and Superoleophilic membranes are more effective for separating the water-in-oil emulsions [136]. These membranes may fail or perform poorly when dealing with oil-in-water emulsions. Therefore, superhydrophilic and underwater superoleophobic membranes are required to address the abovementioned issues.

The superhydrophilic and underwater superoleophobic hydrogel-coated mesh were designed to separate the oil and water mixtures. It can separate the various oil/water mixtures, including vegetable oil, gasoline, diesel, and crude oil/water, with a separation efficiency of >99%. The underwater superoleophobic interface with minimal oil drop affinity prevents the coated mesh from clogging, making it reusable. It is a novel attempt to harness wettability to build next-generation oil/water separation materials, which might be used in industrial oily wastewater treatments and oil spill clean-up. The PAM hydrogel-coated mesh demonstrates underwater superoleophobic behavior with an oil contact angle (OCA) of 155.3° ± 1.8° (Figure 9). When hydrogel coatings touch oil droplets, water is trapped in the rough nanostructures, forming an oil/water/solid interface. These trapped water molecules reduce oil droplet-to-surface interaction and improve separation efficiency [137].

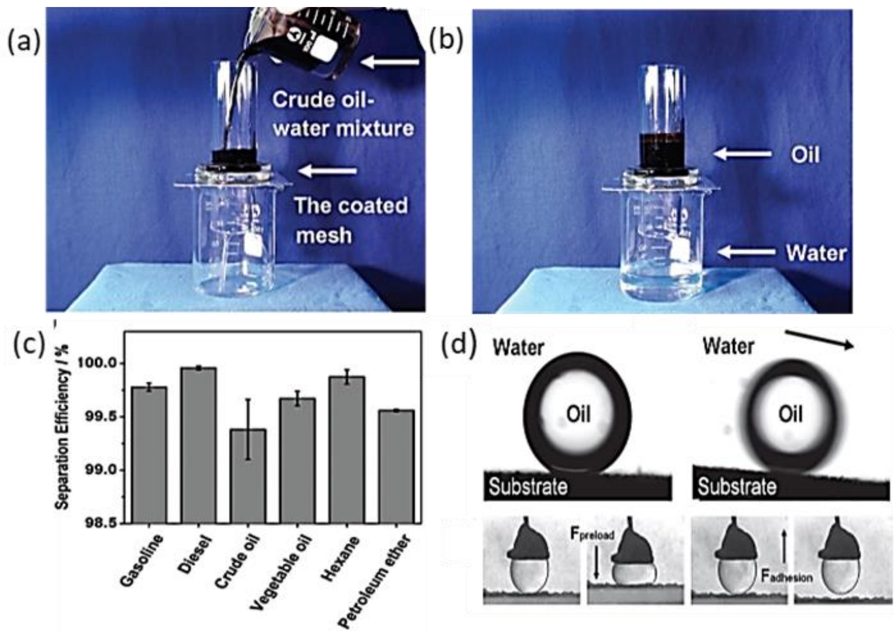

Figure 9. PAM hydrogel-coated mesh oil/water experiments. Mesh pores are 50 µm. (**a**) Coated mesh was fixed between two glass tubes, and crude oil and water were added to the upper tube. (**b**) Water penetrated the coated mesh whereas oil remained in the upper glass tube. (**c**) The oil rejection coefficient of PAM hydrogel-coated mesh for various oils. (**d**) As-prepared PAM hydrogel-coated mesh demonstrates remarkable wettability with underwater superoleophobic and low oil-adhesion qualities [137]. Reprinted with permission from Ref. [137] Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Oil–water emulsion separation was made easier by the super-hydrophilic/underwater superhydrophobic properties of the TiO_2@GO/PEN fiber composite membrane, enhancing its anti-fouling capabilities [138]. The hydrothermal technique followed by UV-initiated polymerization was used to create CuO@PAA composite membrane on the copper mesh. Inorganic CuO rods improved PAA hydrogel's stability and abrasion resistance, whereas water absorbent PAA resin increased its underwater oil repellence. As predicted, the CuO@PAA composite membrane separated kerosene-water, hexadecane-water, soybean oil–water, and rapeseed oil–water mixtures with high efficiencies above 99.90% and excellent water permeation flux of 5700 LMH With a kerosene contact angle of 160.4°, the CuO@PAA membrane proved superoleophobic underwater (Figure 10). CuO@PAA membrane separated oil–water mixtures continuously without fouling.

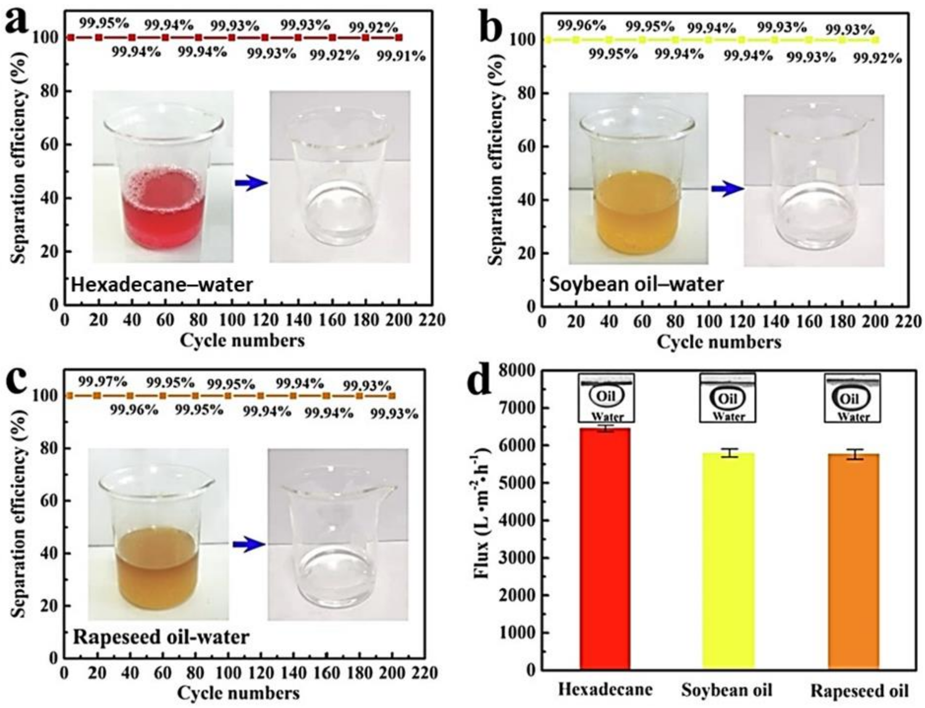

Figure 10. Separation efficiencies of CuO@PAA membrane for various oil–water combinations (**a**–**c**) and water penetration fluxes (**d**). Insets 10a, b, and c show oil–water combinations and filtered water; 5d shows hexadecane, soybean oil, and rapeseed oil on CuO@PAA membrane in water [139]. Reprinted with permission from Ref. [139].

Therefore, the kerosene droplet could quickly separate from the surface at a tilting angle of 2° without leaving any residue, indicating a weak adhesive force between the surface and the oil droplet. In addition, the water contact angle of the CuO@PAA membrane was 0°. It proves that the CuO@PAA membrane was superhydrophilic and had a high-water absorption capacity, which was advantageous for its oil-repellent properties [139]. Recently, a workable self-assembly method was used to synthesize a biodegradable and biomimetic composite membrane with a 2D Voronoi-like BC nanonet skin layer and porous starch fiber matrix. The as-fabricated composite membrane displayed exceptional selective super-wettability due to the cooperative action of the sub-micron-scaled pore size and superhydrophilicity 0°/superoleophobic 150° of the hydrated nanonet skin (Figure 11). Moreover, the composite membrane might serve as a better platform for the separation of immiscible oil–water mixtures and oil–water emulsions due to the permselective interception effect of the nanonet skin layer and the high porosity structure [140].

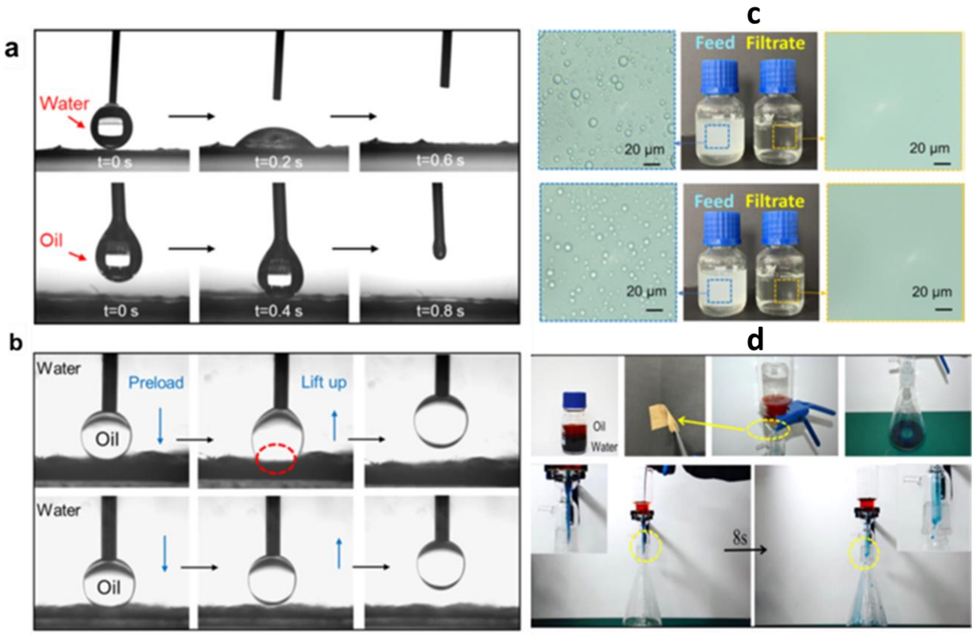

Figure 11. (**a**) Rapid water and oil spread over the membrane as shown by high-speed photography. (**b**) Dynamic images demonstrating the oil repellency and oil adhesion of CSNFMs and BC- CSNFMs while submerged in oil. (**c**) Digital photographs for silicone-in-water SFE (up) and SSE (down) before and after separation. (**d**) Demonstration of separation of immiscible oil-water mixtures. [140]. Reprinted with permission from Ref. [140]

Jin et al. suggested an electrostatic spinning strategy to construct a superhydrophilic/underwater superoleophobic PSA/PVP nanofibrous membrane for oil–water emulsion separation. This superhydrophilic/underwater superoleophobic nanofibrous membrane demonstrated exceptional separation efficiency of 99.7%. Adding 3% PVP to the PSA membrane increased pure-water flux by 835% compared to a pure PSA nanofibrous membrane (220 LMH). The underwater contact angles for all the tested membranes were above 150°. The developed membranes have shown remarkable cycle stability and extraordinary resistance to organic solvent corrosion, indicating their tremendous potential for use in the oil–water separation of wastewater in harsh environments [141]. Xie et al. presented the development of an environmentally friendly and very durable RGO composite membrane for oil/water separation via intercalation of nanoparticles [142]. More recently, the one-step co-deposition of polydopamine and chitosan-tripolyphosphate (CS-TPP) nanoparticles utilizing the ion gel approach made the nylon membrane very hydrophilic and underwater superoleophobic [143]. With an undersea oil contact angle (UOCA) of 179.6°, the obtained superhydrophilicity CS-TPP@PDA@nylon membrane demonstrated good anti-fouling performance by combining the hydrophilic coating of polydopamine and the hydrophilic nanoparticles produced by the ion gel approach. The oil-in-water emulsions' average particle size was 50.9 to 1832.0 nm; the designed membranes were able to separate all the 12 emulsions with a separation efficacy of 97.5%, and for chloroform-in-water emulsions, the separation efficiencies were more than 99.94%. Table 2 summarizes some characteristics and oil–water separation performance of underwater superhydrophilic and superoleophobic membranes and materials.

Through this discussion, it is clear that the separation capabilities of conventional membranes for the treatment of oily wastewater are weak, and they have a short life cycle because of their rapid fouling. Studies in the literature have generally concentrated on constructing sophisticated membranes with excellent separation performance, including high water fluxes, high rejections, and exceptional anti-fouling capabilities. Special wettable membranes have shown a strong tendency to replace conventional membranes for oil/water separations. Special wettable membranes are receiving great importance due to their high fluxes, excellent rejections, and enhanced anti-fouling behavior. Although extensive research has been conducted to develop special wettable membranes, much room is still left to introduce the facile route and stable materials for designing the next-generation membranes. For the scaleup of the special wettable membranes to treat the oily wastewater, membranes must sustain for a longer time in harsh physical and chemical conditions.

Table 2. Comparison of the performance of the superhydrophilic and superoleophobic membranes for oil/water separation.

Materials/Membranes	Filtration Type	Emulsion (Oil-In-Water or Oil/Water Mixtures)	Pressure (Bar)	Water Contact Angle	Underwater Oil Contact Angle	Separation Efficiency	Ref.
polyacrylamide (PAM) hydrogel-coated mesh	Microfiltration	Oil used: Gasoline, diesel, vegetable oil, hexane, and petroleum ether	Gravity	0°	155.3° ± 1.8°	99%	[137]
CuO@polyacrylic acid(PAA)	Microfiltration	Oil used: kerosene–water mixtures	Gravity	0°	160.4°	99.90%,	[139]
Polysulfonamide/ Polyvinylpyrrolidone Nanofibrous Membranes	Microfiltration	Oil used: n-hexane	Gravity	0°	150°	99.7%	[141]
biomimetic BC/starch nanonet membrane.	Microfiltration	Oil used: diesel, vegetable oil, hexane, petroleum ether, and silicon oil	Gravity	0°	150°	99.996%	[140]
TiO_2@GO/PEN FCM	Microfiltration	Oil used: petroleum ether	0.4	0°	162.5°	99%	[138]
FOGE-TA-SSM	Microfiltration	Oil used: kerosene, cyclohexane, n-hexane, n-dodecane, and petroleum ether.	Gravity	0	155	99%	[144]
AL/RGO@PDA	Microfiltration	Oil used: soybean oil, engine oil, n-hexadecane, kerosene, and trichloromethane	-	0°	151°	99.10%	[142]
PVP-UiO-66-NH_2/PAN	Microfiltration	Oil used: n-hexane	Gravity	0°	165.4°	99.2%	[145]
The polyaniline-coated alumina membranes	Microfiltration	Oil used: diesel	1.5	0°	150°	97%	[58]
CFHP/PDA-coated membrane	Microfiltration	Oil used: dichloromethane (DCM), petroleum ether, chloroform, gasoline, hexane, and methylbenzene	Gravity	0°	150°	99.96%	[146]
ceramic membrane with TiO_2 nanowire	Microfiltration	Oil used: Diesel	0.1–0.3	<5°	158°	97%	[147]
MXene@TiO_2/PEN membrane	Microfiltration	Oil used: Isooctane	0.4	0°	155°	99.13%	[148]
CS-TPP@PDA@nylon membrane	Microfiltration	Oil used: Methyl silicone oil, colza oil, or diesel oil	Gravity	0°	179.6°	99.94%	[143]
PVDF@ZnO membrane	Microfiltration	Oil used: n-hexane, petrol, toluene, and diesel	Gravity	0°	162°	99%	[149]

6. Brief Discussion of the Mechanism of the Oil/Water Separation by Using Special Wettable Membranes

Two important phenomena govern the membrane-based separation of oily wastewater: the size exclusion principle and the surface wettability of the membrane [150–152]. While the former plays a significant role in solvent passage through the membrane channels, the latter determines the affinity of the surface for water or oil molecules. The size exclusion principle provides an avenue to discriminate between oil and water molecules based on size. Tiny water molecules tend to pass through depending on the pore size, while bulky oil molecules are blocked. However, in some instances, dispersed oil droplets can squeeze and penetrate through the pores and stop the water molecules from passing through a phenomenon known as pore plugging [153]. When this happens, a decline in flux and oil rejection is observed. Thus, controlled just by the size exclusion, the fouling of the membrane would be faster. Thus, to minimize this, the surface roughness and the surface energy of the oily wastewater treatment membranes must be controlled to either make them hydrophilic/oleophobic or hydrophobic/oleophilic. Even the stratified oil/water mixtures in which the droplet size is greater than 20 μm can be easily separated using superwettable materials with a pore size greater than a few tens of micrometers. In superhydrophilic surfaces, the water droplet spreads rapidly and passes due to its strong interaction with the surface where the oil is rejected. The superhydrophilic surfaces of the membranes usually possess high surface energy polar groups, including the sulfonic acid, hydroxyl, aldehyde, amino, and carboxyl groups [154]. The superhydrophobic and superoleophilic designed membranes work exactly opposite to the superhydrophilic and underwater superoleophobic membranes as these membranes possess low surface energy, which allows the rapid spread of the oil on it and blocks the water. Thus, the special wettable membranes can easily filtrate or adsorb the relevant phase according to the designed surface wettability [34]. However, special wettable surfaces with loose pores are more suitable for the stratified mixtures, but when the emulsified droplet size is tiny, the special wettable membranes with the loose pores may not much effective. Therefore, more rigorous control of the pore size is also required, along with the special wettability, to achieve the required separation efficiency.

7. Challenges and Future Perspective

From the discussion, it is clear that extensive research is going on in the treatment of oily wastewater, which usually represents the oil-in-water emulsion. Special wettable membranes are also dealing with the subject of water-in-oil emulsions, which have industrial significance. Apart from the extensive progress in the field, many challenges are associated with the special wettable membranes for oil/water separations. Challenges are always opportunities to solve the problem effectively and bring the special wettable membranes to the next stage and near the industrial and environmental demands. Numerous studies in literature have shown that special wettable membranes have been designed that work under gravity with exceptionally high flux. However, the membranes that show high flux under gravity are usually more effective for treating the layered oil/water mixtures but may not be much effective for separating the emulsions. Therefore, more rigorous control of the pore size is required to have a synergistic effect of special wettability and the size exclusion principle to treat the emulsified oil/water feed [155]. One advantage of special wettable membranes over adsorbent is separating the layered oil/water mixture is that the adsorbent can saturate after some time, then the adsorbent should be regenerated for the next cycle [156] and special wettable membranes are advantageous for continuous oil/water separation, but one of the major challenges is associated with the fouling of the surface. Even during the layered oil–water separation, some challenges may appear apart from their special wettability. For example, in gravity-based separation, while using the superhydrophobic membranes, the water may make the first layer due to gravity and prevent the passage of the light oil. This issue can be resolved by appropriately designed separation assembly. The surface energy is usually lowered by using the fluorine-containing organic linker to enhance the superhydrophobicity of the membranes. The fluorine-containing linkers may be responsible for secondary environmental contaminants. Therefore, there is a need to find environmentally friendly low surface energy materials to tune the characteristics of the membranes. The special wettable membranes are less explored for complex systems, such as produced water, highly viscous components, and different surfactant stabilized oils, in which surfactant can also perform its role in fouling the membrane surface.

Furthermore, more efforts are required to design the solvent resistance membranes as some polymeric membranes lack the appropriate chemical stability. For instance, poly(ethylene terephthalate) offers good resistance to various solvents, chlorine, and acids [157]. Chinmoy Bhuyan et al. designed the organic solvent-resistant cellulose nanofiber-poly(ethylene terephthalate) nanocomposite membrane and used it to treat the petroleum industry wastewater [158]. Sustainable sources have also been used to develop the NF membranes, which is a new direction to design the membranes using environmentally friendly processes [159]. Similarly, sustainable sources have been used to develop hydrophobic thin film composite NF membranes, which offer good solvent resistance [160]. Furthermore, the stability of the membranes for oil/water separation can be enhanced by crosslinking the polymers [161].

Therefore, more efforts are required to investigate the mechanisms of the separation of the membranes for complex oil/water systems, and more evaluation of the membranes is necessary for real oily wastewater instead of simulated ones to see the industrial practicality of the special wettable membranes.

8. Conclusions

In summary, this review discusses the recent progress of special wettable membranes for the oil/water separation application. Oily wastewater has become a severe environmental concern due to rapid industrialization and periodical oil spills. The membranes faced various kinds of fouling during the operation, such as complete blocking, intermediate blocking, standard blocking, and cake layer formation. The fouling with the oil is more complex as the liquid drops under pressure can squeeze and merge to make a tighter layer which results in a sharp decline in flux, and high pressure can have a negative impact on the separation efficiency as the liquid drop under pressure can squeeze and pass through the pores which are smaller than droplet size. Special wettability of the membranes is one of the critical solutions to enhance the performance of the membranes. The various wettability models based on the contact angle have been presented, including the Young model for smooth surfaces, the Wenzel model, and the Cassie–Baxter model for rough surfaces. Based on wettability, membranes can be divided into two major categories. One is oil selective, which is defined by its superhydrophobic and superoleophilic nature. These membranes selectively allow the oil to pass and reject the water. The second category of the special wettable membrane is the water selective, which is superhydrophilic and underwater superoleophobic. This sort of membrane selectively allows the water to pass and reject the oil. Although extensive work can be seen in the literature, the stability of the special wettable membrane is still a concern for the scale-up of these membranes.

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