Water Air Soil Pollut (2024) 235:80
https://doi.org/10.1007/s11270-023-06864-x

Multifunctional Smart Nano-membranes for the Removal of Oil-Based Pollutants from Marine Sources: A Tool for Sustainable Environment

Zaeem Bin Babar · Komal Rizwan · Shahid Munir

Received: 19 September 2023 / Accepted: 26 December 2023 / Published online: 12 January 2024

Abstract Oil–water separation is necessary to mitigate the impacts of oily wastewater released from industrial processes, frequently occurred oil spillages during transportation, and oil and gas exploration on ecology and environment. Since oil and water are immiscible, the solid surfaces can be engineered using various nanomaterials to alter their wettability characteristics for effective oil–water separation. In this context, carbon-based membranes (i.e., graphene oxide (GO), carbon nanotubes, and carbon nanofibers) have received significant attention in the past decade or so. Additionally, their surficial modifications with a variety of nanomaterials (i.e., MXenes, MnO_2, TiO_2, ZnO, MoS_2) improved their wettability, permeation flux, and selectively for various oil–water emulsions which renders them efficient to remove oil or water from oil–water emulsions via adsorption, absorption, and simple filtration. Various types of modified carbon-based membranes have been developed and successfully applied for separating oil–water emulsions in the laboratory. In addition to their excellent separation performance, they exhibit tremendous mechanical durability and regenerative properties for their extended reuse. Consequently, owing to these principal characteristics, they can be considered as promising candidates for efficient oil–water separation. However, their utilization is still limited for commercial-scale applications due to their low cost-effectiveness and reusability over longer periods of time.

Keywords Carbon-based membranes · Nanomaterials · Oil–water separation · Graphenes

1 Introduction

Oily wastewater is released from several industrial processes. Considering global water pollution and its substantial health and environmental impacts, the treatment of oil-based polluted water is critical not only owing to its release in enormous quantities from various industrial activities but also due to its complicated composition which comprises a variety of oily substances. Additionally, such complex oil–water mixtures are hard to handle. The common industrial sources of oily wastewater include mining operations, food processing activities, textile manufacturing, oil and gas exploration and processing, metal plating, and steel manufacturing processes (Chen & Zhi-Kang, 2013). For instance, in a conventional mining process, approximately 140,000 L per day of oil-polluted water is released (Guerin, 2002).

Z. B. Babar · S. Munir
Institute of Energy and Environmental Engineering,
University of the Punjab, Lahore 54590, Pakistan

K. Rizwan (✉)
Department of Chemistry, University of Sahiwal, Sahiwal,
Pakistan
e-mail: drkomalrizwan@uosahiwal.edu.pk; Komal.rizwan45@yahoo.com

Additionally, oil spill and leaks during transport via seas and oceans are another source of marine water contamination and impart negative effects on aquatic life and ecological conditions along with dissipation of a worthy energy source (Chen & Zhi-Kang, 2013). The various possibilities of oil contamination are demonstrated in Fig. 1. The extent of the detrimental influence on marine life largely depends on several factors including the type and composition of oil spill, variety of species, and natural resistance level of each affected species (Li et al., 2016). Significant damaging effects of oil spills on marine wildlife, invertebrates, mammals, and microbial communities have been reported (Bastida et al., 2016). To mitigate these problems, different techniques at industrial scale and conventional materials at laboratory have been utilized and developed, respectively, for the treatment of oil-based polluted wastewater. For instance, on industrial scale, skimmers and/or booms are utilized to treat oil–water mixtures; however, the utilization of these devices is appreciably energy intensive, requiring high pressures and electricity consumption (Ventikos et al., 2004). Furthermore, various substances with high porous morphology are generally employed such as sponges and foams (with considerable affinity to remove oil from oil-based wastewater via absorption) (Calcagnile et al., 2012; Zhu et al., 2013). However, they offer certain disadvantages including low separation efficiency (i.e., absorption capacity) and selectivity. In addition, their usability is limited due to difficulty in their regeneration (i.e., separation of absorbed oil from the employed materials). Therefore, they are either dumped or combusted which cause secondary pollution in the form of emission of hazardous pollutants and gases in atmosphere and soil toxicity (Adebajo et al., 2003). For laboratory-scale studies, the investigations using conventional methods (i.e., adsorption, bioremediation) for treating oil–water mixtures have also been presented and showed tremendous promise; however, they have certain drawback such as low effectiveness and complex mechanisms (Pan et al., 2019; Yang et al., 2020). Hence, fabrication of materials possessing low cost, facile preparation procedures, eco-friendliness, high oil–water separation efficiency, excellent reusability, and simple regenerations, energy efficient, etc., along with capability to treat oil-based polluted water with high throughputs (i.e., high permeation flux), is urgently required to address this global challenge.

One of the effective techniques for water purification is membrane separation. It has several benefits such as simple operation, less energy intensive, and high separation efficiency (Cheng, Barras, et al., 2020). Huge literature data is available regarding the assessment and evaluation of membranes specifically carbon-based membranes including GO and carbon nanotubes in water purification applications (Zhang et al., 2020). Their enhanced surface features (i.e., high surface areas) and hydrophilic properties make them effective materials for efficiently separating water-miscible pollutants from contaminated water (Han & Peiyi, 2019; Zhang et al., 2019). Additionally,

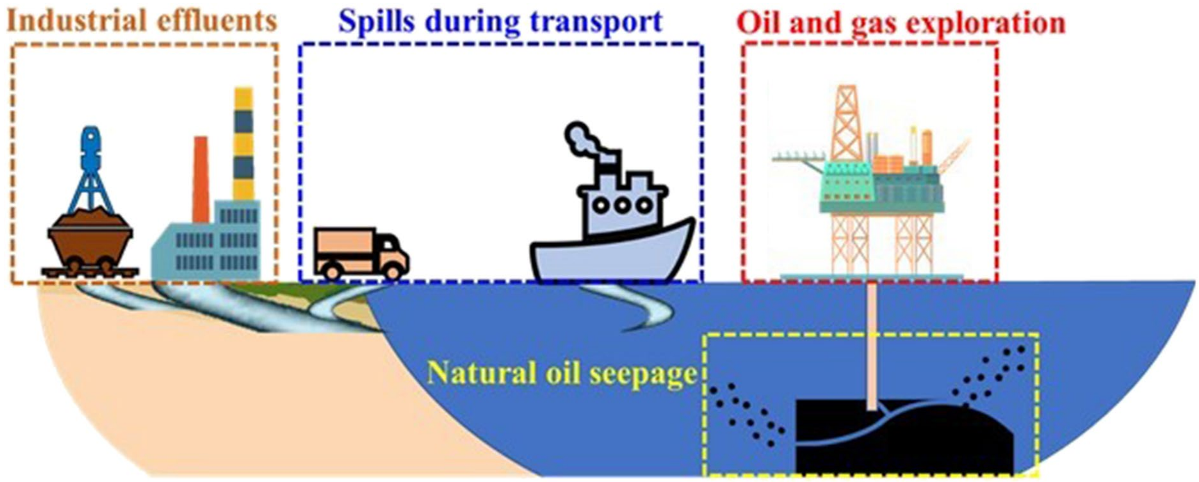

Fig. 1 Various sources of oil contamination in ecosystem

their affinity for the abatement of desired contaminants from polluted water can be increased by modifying their structure via interfacial alterations, covalent and/or non-covalent bonds, etc. (Choi et al., 2020; Hu et al., 2022). In general, there are four categories of carbon-based membranes;(1) superhydrophobic, (2) superhydrophilic, (3) Janus, and (4) smart (An et al., 2018; Liu et al., 2020; Liu, Weifu, et al., 2018; Ma et al., 2017; Qu et al., 2020; Zhao et al., 2020). Among them, superhydrophilic carbon-based membranes are extensively investigated owing to their extraordinary antifouling resistance and wettability characteristics (Jayaramulu et al., 2019; Meng et al., 2018; Serhan et al., 2019). Additionally, they conveniently attain the desired oil–water mixture separation by simply prewetting with their responding solvents (Fan et al., 2019; Guan et al., 2018; Noamani et al., 2019; Pan et al., 2019). Furthermore, they are relatively facile than their counterparts. Moreover, their intrinsic chemical functionalities furnish them to effectively abate hazardous pollutants including dyes bacteria from polluted water (Han & Guo, 2021; Ye et al., 2021).

Numerous review publications can be found in the literature with respect to the applications of different membranes and material for oil–water separation (Dmitrieva et al., 2022; Rasouli et al., 2021; Yue et al., 2019; Zhang et al., 2022). For instance, recently in 2019, Yue and colleagues analyzed fiber-based membranes with respect to design and fabrication strategies (Yue et al., 2019). Rasouli and coworkers primarily focused on discussing mesh, porous, and film-based membranes in treating oil–water emulsions (Rasouli et al., 2021). In another review, Dmitrieva and colleagues put efforts to consider the applicability of synthetic polymeric membranes comprising of polysulfone, polyethersulfone, polyacrylonitrile, and polyvinylidene fluoride for separating oil–water mixtures (Dmitrieva et al., 2022). In a recent article, Zhang and colleagues comprehensively reviewed various category of membranes based on substrate such as metal mesh, gel, and biomass, in treating oil in water mixtures (Zhang et al., 2022).

However, to the best of our knowledge, no specific review in the literature is available relevant to the application of carbon-based membranes (GO and associated derivatives, carbon nanotubes, and carbon nanofibers) and their modified forms. Despite the fact that membrane separation and purification technology is well established and matured; nevertheless, the progress and innovation in carbon-based membranes and corresponding modifications and their effective utility in oil in water separation applications deserve to be reviewed in the context of material modification via nanoparticles, performance characteristics, and commercial utilization. Therefore, herein, the recent advancements specifically related to carbon-based membranes modified with wide range of nanomaterials for separating oil–water media have been summarized and thoroughly discussed. Initially, surface wettability, contact angles, and phenomenon of oil–water separation are discussed. Afterwards, a comprehensive review of performance (permeation flux and oil–water separation efficiency), wettability, surface composition, properties, selectivity, and regenerative abilities is presented. Lastly, research gaps, outlook, and conclusions are discussed.

2 Surface Wettability, Contact Angles, and Process of Oil–Water Separation

Recent studies relevant to oil–water separation have typically emphasized material wettabilities (intrinsic nature of the surface that allows liquid to distribute over a surface and is generally measured by contact angles) including superb-hydrophilic (water loving) and superhydrophobic (water repellent) and remarkable oleophilic (oil loving) and oleophobic (oil repellent) properties (; Wang & Gong, 2017; Xue et al., 2014). Wetting nature of liquid on surface is determined through the contact angle of the liquid made on surface. If contact angle would be larger than the wettability, then it shall be low and vice versa. In water–solid–air interface, if water contact angle is lower than 90°, then the surface may be hydrophilic, and if water contact angle is lower than 5°, then the surface shall be superhydrophilic. Superb-hydrophobic materials possess water contact angles greater than 150°, while water contact angle of greater than 90° shows that surface is hydrophobic (Fig. 2A). In case of oil–solid–air interface, if oil contact angle is ≤90° and ≤5°, then surface shall be considered as oleophilic and superoleophilic, respectively. And if oil contact angles are ≥90° and ≥150°, then surfaces are oleophobic and superoleophobic. So overall it can be concluded that wetting surfaces are the ones which possess contact angle less than 90° and

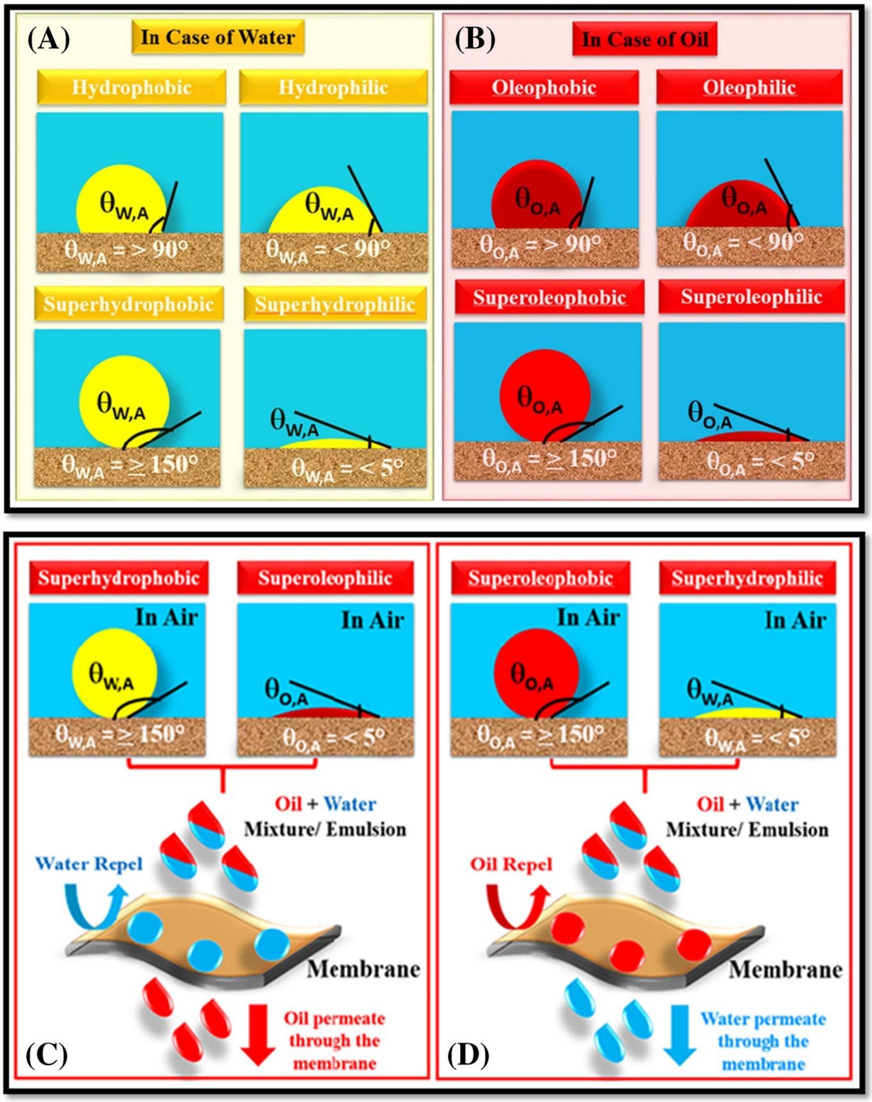

Fig. 2 Classification of different wetting, non-wetting, and super-wetting states in case of water (**A**) and oil (**B**). Possible wetting states of porous membrane/materials for oil–water separation applications. Superhydrophobic and superoleophilic (**C**) and superoleophobic and superhydrophilic (**D**). Reprinted with permission from (Baig et al., 2022). License # 5682000831658

non-wetting surfaces keeps contact angle greater than 90° (Fig. 2B). The geometry and chemical composition of the surface significantly affects the distribution (wetting and/or dewetting) of liquid on it. Consequently, these two parameters can be tuned to develop a material with desired wetabilities (superb and/or poor). Superhydrophobic/superoleophilic membranes have potential to separate water from oil, and they can block water and permits only oil to pass through membrane (Fig. 2C), while superhydrophilic/superoleophobic allows water to pass through membrane and block oil to pass (Fig. 2D). Therefore, selective oil water separation can be carried out by employing materials with smart surfaces and great wettability features. Thereof, it is highly needed to develop materials with great wettability for high performance of oil–water separation (Ali et al., 2020). The superhydrophobic/superoleophilic membranes are more efficient in separation of emulsions having high water content because they repel water and absorb oil-based contents. Various approaches are employed for synthesis of superhydrophobic/superoleophilic membranes like dip coating, polymer grafting, spray-coating, and vapor deposition (Fang et al., 2016; George & Verma, 2022). The literature survey exhibits that over the last decade, extensive studies were performed to evaluate the oil–water separation using superhydrophobic materials (Wong et al., 2013;

Lu & Yuan, 2017; Xue et al., 2014). Hydrophilic surfaces exhibit high surface tension in comparison of water. And it is challenging to fabricate superhydrophilic surfaces due to unavailability of any material which shows high surface energy in comparison of water and lowers surface energy than oil.

3 Application of Smart Carbon-Based Membranes in Oil–Water Separation

3.1 Graphene-Based Nano-membranes

Among carbon-based nanomaterials, graphene has stable configuration and is composed of layered graphite arranged in a discrete manner. In addition, carbon atoms are organized in a hexagonal structured network. GO is a derivative of graphene formed as a result of dispersion of graphite oxide in a suitable solvent or solution such as basic and polar fluids to generate its monolayer. The primary distinction between GO and graphite oxide lies in the distance between planes of their layered atoms. Furthermore, another derivative of GO is reduced graphene oxide (rGO) which is formed by the removal of oxygen from GO via physicochemical methods (Fig. 3). The rGO exhibits superior conductive properties to graphene and GO (Al-Anzi & Siang, 2017).

Fouling of the membrane is a critical drawback owing to its hydrophobicity. As a result, the operational life of the membrane becomes short. Therefore, the operational performance (i.e., hydrophilicity) of the membranes can be enhanced using various modifications. In the recent years, scientists and researchers relevant to the scientific area of waste and wastewater treatment focused on developing membranes based on graphene and its derivatives (i.e., GO) (Yin et al., 2021). These materials were found to be effective due to their intrinsic leanness and overlaid formation which augment membrane's hydrophilicity, permeation, and therefore, the treatment rate of water and wastewater. Summary of separation performance (permeation flux, separation efficiency), wettability, selectivity, and reusability of GO-based nanomembranes for oil–water separation is presented in Table 1.

Jiang and colleagues utilized freeze-casting and chemical vapor deposition methods to develop a biopolymeric membrane of T-sodium aligate/lignin/rGO-trimethoxymethylsilane (MTMS) with excellent hydrophobic characteristics. During the preparation, rough surfaces similar to those hedgehog bearing apples were formed owing to the MTMS incorporation (Jiang et al., 2022). The water contact angle (WCA) was 161° which provides evidence of extraordinary hydrophobic nature of the resultant membrane. Moreover, GO was reduced due to intrinsic property of lignin. The membrane exhibits tremendous reusability and was able to withstand 10 oil–water separation cycles (An et al., 2018). It was primarily due to lower surficial energy associated with rGO in the porous 3D framework of membrane.

In another study, a weather and highly chemically resistant membrane with fibrous nature was synthesized using rGO, transition metal carbides, nitrides, carbonitrides (MXene), and polyphenylene sulfide

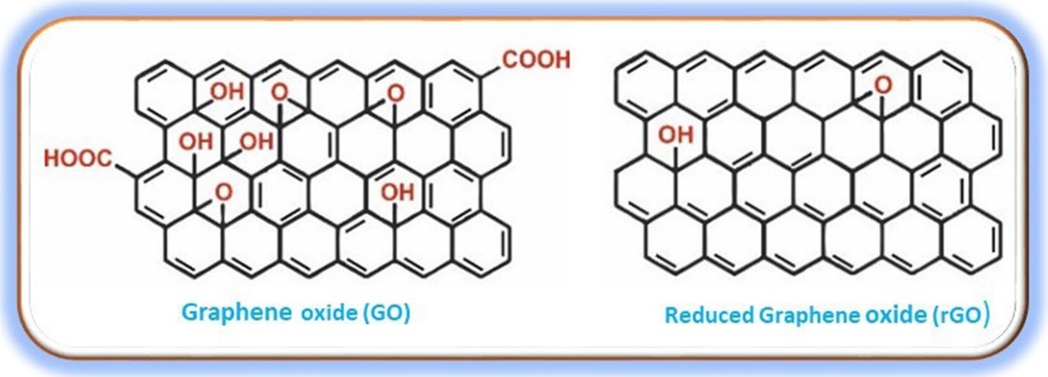

Fig. 3 General representation of graphene oxide and reduced graphene oxide structures

Table 1 Summary of separation performance (permeation flux, separation efficiency), wettability, selectivity, and reusability of GO-based nano-membranes for oil–water separation

GO-based nano-membranes	Fabrication process	Surface area (m^2 g^{-1}) & porosity (%)	Wettability	Permeation flux (Lm^{-2} h^{-1} bar^{-1})	Separation efficiency (%)	Selectivity	Regeneration cycles	References
Biopolymeric aerogel membrane (T-sodium aligate/lignin/reduced graphene oxide (rGO)-trimethoxymethylsilane (MTMS))	Freeze-casting and vapor deposition	-	Hydrophobicity (contact angle 161°)	-	96.7	Pump oil, isooctane, chloroform, dichloromethane, n-hexane, xylene	10	Jiang et al., (2022)
rGO/MXene($Ti_3C_2T_x$)@PPS fibrous membrane	Melt blowing technique	-	Hydrophobicity (contact angle 145°)	11502	99.98	Kerosene oil, soybean, toluene, dichloromethane	10	Wang et al., (2022)
Speolite@MnO_2/rGO	Hydrothermal and vacuum distillation	-	Hydrophobicity (contact angle 160°)	923	90	Oilfield wastewater	15	Xiao et al., (2022)
MoS_2-rGO alumina membrane	Thin-film deposition	-	Hydrophilicity (contact angle 74.9°)	102.3	92.5	Synthetic oily wastewater	-	Othman et al., (2022)
Lignin based rGO/glass fiber membranes	Hydrothermal reduction and vacuum filtration	-	Hydrophobicity (contact angle 151°)	2410.3	99.4	Soybean, engine oil, kerosene, n-hexadecane, toluene, trichloromethane	10	Xie et al., (2022)
Polyvindiline fluoride/rGO/polydimethylsiloxane	Electrospinning	-	Hydrophobicity (contact angle 144°)	6762.5 5280	>93	Toluene, trichloromethane	20	Zhou et al., (2022)
Tannic acid crosslinked GO	Vacuum filtration	-	Hydrophilicity & oleophobicity	-	91.7	-	-	Singhal et al., (2020)
Polysulfone-based mixed matrix membranes (PS-MMMs) consisting of GO and aspartic acid	Phase inversion	-	Hydrophilicity (contact angle 64°)	1375	98	-	2	Abdalla et al., (2020)
Membrane based on GO, rGO, and polybenzimidazole	Blade coating & phase inversion	-	Hydrophilicity (contact angle 45.8–61.3°)	91.3 ± 3.4	99	-	4	Alammar et al., (2020)

Table 1 (continued)

GO-based nano-membranes	Fabrication process	Surface area (m^2 g^{-1}) & porosity (%)	Wettability	Permeation flux (Lm^{-2} h^{-1} bar^{-1})	Separation efficiency (%)	Selectivity	Regeneration cycles	References
Fibrous nano-membrane from polyvinylidene fluoride and graphene	Electrospinning	- & 92.8	Hydrophobicity (contact angle 140.1°)	23794 ± 928	99.8	Span 80 surfactant-stabilized oily water emulsions	-	Zhang et al., (2021)
Membrane based on rGO, polydopamine, and perfluorodecanethiol	Two-step immersion	-	Hydrophobicity (contact angle 156°)	-	-	Chloroform	-	Cheng, Barras, et al., (2020)
Membrane based on chitin nanoparticles, rGO, and dopamine	Vacuum filtration	-	Hydrophilicity (contact angle 44.9°)	135.6	97.5	-	5	Ou et al., (2019)
Membrane based on sepiolite, GO, and polyvinylidene fluoride	Vacuum filtration	-	Hydrophobicity (contact angle 150–157°)	531.7	99	Mesitylene, kerosene, decane, and petroleum ether	-	Yu et al., (2019)
Membrane based on GO and polyethersulfone	Phase inversion	- & 89.1 & 84.1 for flat sheet and hollow fiber membranes	Hydrophilicity (contact angle 71.4° and 49.8° for flat sheet and hollow fiber membranes)	95.12 ± 8.7 & 196.1 ± 3.2 for flat sheet and hollow fiber membranes	50 & 98 for flat sheet and hollow fiber membranes	-	-	Junaidi et al., (2021)
Membrane based on TiO_2, sulfonated GO, and Ag nanoparticles	Vacuum deposition	-	Hydrophobicity (contact angle >150°)	53	99.6	Toluene, gasoline, heptane, and chloroform	10	Qian et al., (2018)
GO-mixed cellulose ester membrane functionalized with polydopamine	Vacuum filtration	-	Hydrophilicity (contact angle 43.8° ± 2.2)	60	96	Toluene	4	Z. Liu et al., (2018)
Membrane based on rGO, SiO_2, and dopamine	Vacuum filtration	-	Hydrophilicity (contact angle 14–64°)	322–647	>99	Pump oil, gas oil, soybean oil, and diesel oil	8	Liu et al., (2020)

(PPS). The operation of developed membrane was based on Joule heat and solar irradiation effects (Wang et al., 2022). The membrane exhibited oil separating efficacy of >97% via sorption process. Moreover, the membrane performance was persistent under harsh conditions such as strong acidic and basic environment. In the case of dichloromethane–water emulsion, the separating flux was 11,502 Lm^{-2} h^{-1}. Additionally, the resultant membrane showed good electrical conductance and shield efficacy from radiation equivalent to 61.9 dB (Fan et al., 2019). An economical membrane based on GO was synthesized via vacuum filtration technology and applied it for treating synthetic oilfield samples (Singhal et al., 2020). It possessed excellent hydrophilic and oleophobic properties. Initially, cross-linking between the sheets of GO and tannic acid was performed to increase structural and mechanical strength and was able to hold out against high water pressures. Additionally, it was observed that chemical oxygen demand (COD) deceased to 91.67% with simultaneous decrease in total dissolved and suspended solids (TDS and TSS) and turbidity (Singhal et al., 2020). In a recent study, the authors developed polysulfone-based mixed matrix membranes (PS-MMMs) by phase inversion. These membranes primarily consisted of aspartic acid and GO and performed well in oil and water separation (Abdalla et al., 2020). They exhibited high permeation, oil retention, and fouling resistance even at extremely low concentrations of GO (i.e., 0.05–2 wt.%) (Abdalla et al., 2020). With the further increase in concentrations, no significant change in the removal efficiency was observed. An appreciable increase in oil retention was observed and found to be 97.9%, respectively, as compared to pristine membrane (Abdalla et al., 2020). Also, permeability was reported to be enhanced by approximately 97%. Furthermore, fouling resistance was increased as evident from steady decrease in flux (i.e., 90% after two cycles) (Chen & Zhi-Kang, 2013). The amino and carboxylic moieties in the nano-membrane were accountable for elevated hydrophobic and fouling resistant properties. Alammar and colleagues fabricated nanocomposite membranes based on GO, rGO, and polybenzimidazole by blade coating and phase inversion methods and utilized them for wastewater released from petrochemical industry. The presence of GO in the membrane enhanced its mechanical strength (Alammar et al., 2020). The oil removal efficiency was approximately 99% owing to the integration of GO in the gridded structure of polybenzimidazole with significant permeability equivalent to 91.3 ± 3.4 Lm^{-2} h^{-1} bar^{-1}. These membranes were very effective in separating oil from industrial waste streams with high salt concentrations. Zhang and colleagues manufactured highly fibrous nano-membrane from polyvinylidene fluoride and graphene through electrospinning technique and employed it for separating oil from surfactant-stabilized water (Zhang et al., 2021). The results showed that the oil abatement efficiency was 99.8% which were primarily due to enhanced porosity (i.e., > 92.8%) and permeating flux (i.e., 23794 ± 928 Lm^{-2} h^{-1} bar^{-1}). Thus, it proved to be an excellent nano-membrane for separating oil in wastewater treatment. Moreover, it exhibited water and oil contact angels of 140.1° ± 1.1° and 0°, respectively, along with appreciable hydrophobicity. A recent study utilized a facile method to prepare a membrane based on rGO and polydopamine modified with 1H, 1H, 2H, and 2H-perfluorodecanethiol and tested it for oil–water separation. It effectively removed chloroform from polluted water due to its excellent oleophilic (i.e., hydrophobic) nature (Baig, Alghunaimi, & Saleh, 2019). Thus, it can be considered as a promising membrane for oil–water separation. The manufactured membrane exhibited a water contact angle of approximately 156°. By applying Cassie–Baxter model, it was observed that around 7% and 93% of the contact areas were between water droplet and the solid surface and water droplet and air, respectively (Cheng, Sun, et al., 2020). In another study, a composite membrane based on chitin nanoparticles and GO was manufactured using vacuum assisted filtration. Additionally, it was modified using dopamine. In this membrane chitin nanoparticles were homogeneously distributed within GO sheets (Alammar et al., 2020). The synergic combination of pointed channels of chitin nanoparticles and presence of dopamine significantly increased the permeation rate, membrane's hydrophilic nature, and hence, the oil–water separation efficiency. As the volume ratio of GO to dopamine added chitin nanoparticles increased from 1:1 to 1:4, the permeation water rate enhanced from 8.8 Lm^{-2} h^{-1} to 135.6 Lm^{-2} h^{-1}. Additionally, the oil and dye rejection ration were found to be 97.5% and greater than 97%, respectively, for composite membrane synthesized with a volume ratio of GO to dopamine added chitin nanoparticles equivalent to 1:4 (Ou et al., 2019). Furthermore, it showed reasonable usability by undergoing 5 regenerations with sustained separation efficiency. Thus, the practicality of it is evident for effective oil–water separation and pollution abatement from polluted waters (Ou et al., 2019). Yu and colleagues fabricated membrane consisted of sepiolite and GO for treating polluted water (Yu et al., 2019). Results exhibited that membrane was highly efficient in the separation of oil from oil–water solutions owing to excellent oil–water selectivity. It also proved to hold extraordinary mechanical stability and selectivity in harsh operating conditions (i.e., underwater functioning). Furthermore, for the case of pure water, the permeation flux significantly accelerated from 7.2 $\mathrm{Lm^{-2}\ h^{-1}\ bar^{-1}}$ (GO membrane) to 531.75 $\mathrm{Lm^{-2}\ h^{-1}\ bar^{-1}}$ (sepiolite and GO membrane). Moreover, it is important to mention that membrane exhibited multiple functions including appreciable abatement of dyes such as methylene blue and Congo red and hazardous heavy metals such as Fe^{3+} and Cu^{2+}. Junaidi and colleagues synthesized composite membrane of two different orientations (flat sheet and hollow fiber) based on GO and polyethersulfone and analyzed their respective oil–water separation efficiency (Junaidi et al., 2021). Also, the influence of GO weight percentage (0.5% and 1.0%) was investigated. It was found that morphological characteristics such as pore sizes of flat sheet and hollow fiber composite membranes were appreciably different even though the GO content was same in both composite membranes. For both flat sheet and hollow fiber membranes, the water contact angle was appreciably decreased from 74.8° and 71.4° to 42.2° and 49.8°, respectively. In addition, the composite membranes with GO weight content of 1.0% GO, the permeation flux increased by 100% and 350% for flat sheet and hollow fiber membranes (Junaidi et al., 2020). Hollow fiber composite membranes exhibited oil rejection equivalent to 99% higher than 50% observed for flat sheet membrane (Junaidi et al., 2020). Although hollow fiber membrane comprised of small pore size, still, high oil rejection might be owing to better flow dynamics. In the case of flat sheet membrane, low oil rejection was due to large pores, thus allowing more oil to pass through it. This study concluded that shape and orientation of the membrane have significant effects on membrane performance (oil–water separation and hydrophilic character) and properties such as pore size (Fan et al., 2019). Furthermore, it was found that hollow fiber membrane offered several benefits including high flux, oil–water separation efficiency, and oil rejection. Therefore, they can be considered as an appropriate option for commercialization.

A variety of graphene-based nanomaterials have been tested for oil–water separation. Yet, nanomaterials synthesized in a one-step possessing a good capability in separating oil–water emulsion with simultaneous soluble pollutant abatement are scarce. Qian and colleagues fabricated a membrane using TiO_2, sulfonated GO, and silver (Ag) nanoparticles and exhibited a strong photocatalytic efficiency for methylene blue under UV light along with high oil–water separation efficiency (Qian et al., 2018). It is further reported that it possessed extraordinary strength at the contact angle of >150° with water. Furthermore, separation efficiency was sustained till 10 successive runs. A coating method to develop a GO-based membrane with excellent mechanical strength was used and applied it for oil–water separation. The mixed cellulose ester membrane (MCEM) was functionalized with polydopamine which acted as a lining agent and bonded covalently with MCEM (Guan et al., 2018; Liu, Yanlei, et al., 2018). Afterwards, GO sheets were coupled with functionalized MCEM via vacuum filtration. The resultant membrane was then utilized for oil–water separation and found to be efficient in separating oil in water emulsions. Moreover, it was found to be reusable for four successive cycles. Additionally, a highly porous nanohybrid membrane comprising of GO and SiO_2 with incorporating ethylene diamine as cross-linker was fabricated. Due to the presence of nano-sized channels induced by incorporation of SiO_2 between the layered structures of graphene, the membrane demonstrated augmented flux, separation efficiency, and oil retention. The hydrophilicity of the membrane was increased owing to the build-up of ethylene diamine on the membrane surface (Liu et al., 2020). Besides, it efficiently removed oil and contaminated dyes from polluted water.

Generally considering oil–water separation, the wettability and permeation of any membrane are a function of chemical functionalities located on their surfaces and their rough structural frameworks. In case of GO-based membranes, the hydrophobic and hydrophilic water contact angles were ranged from 140.1° to 161° and 14° to 74.9°, respectively (Liu et al., 2020). The corresponding values of permeation were in the range between 923 Lm^{-2} h^{-1} bar^{-1} and 23,794 Lm^{-2} h^{-1} bar^{-1} and 53 Lm^{-2} h^{-1} bar^{-1} and 1375 Lm^{-2} h^{-1} bar^{-1}, respectively. Also, their separation efficiencies for a wide range of model oil–water emulsions including pump oil, kerosene oil, toluene, and dichloromethane were reported to be greater than 90% (Table 1). Considering hydrophobic GO-based membranes, the biopolymeric aerogel membrane comprising of sodium alginate, lignin, rGO, and MTMS exhibited maximum hydrophobicity with water contact angle of 161°. This high contact angle was due the presence of hydrophobic groups including C=C and Si-C, located on its surface associated with intrinsic chemical composition of its chemical constituents. In addition, the rough structural framework primarily provided by rough lignin particles with superior air cushion also assisted the hydrophobic nature of the membrane. Among reported GO-based membranes, the highest permeation flux was 23794 Lm^{-2} h^{-1} bar^{-1}, found for fibrous nanomembrane comprising of polyvinylidene fluoride and grapheme. Due to the incorporation of graphene nanosheets within the structure of fibrous membrane, pore size distribution augmented (porosity > 92.8%) which further increased the oleophilic permeation, and the corresponding separation efficiency for Span 80 surfactant-stabilized oily water emulsions was 99.8% (An et al., 2018). Focusing on the regeneration capabilities of GO-based membranes, the composite membrane comprising of polyvinylidene fluoride, rGO, and polydimethylsiloxane underwent 20 regeneration cycles (the highest number among reported GO-based membranes) successfully without any significant change in permeation flux (Junaidi et al., 2020). This superior reusability of this membrane could be linked to high mechanical integrity with the tensile strength of 3.165 MPa and fibrous nature.

3.2 Carbon Nanotube–Based Membranes

Carbon nanotubes are typically 2-D nano-sized materials possessing cylindrical graphitic-layered framework. They are commonly categorized in two classes, namely, "single walled" and "multiwalled" (Fig. 4). Due to their excellent structural robustness, thermal durability, and conductive properties, they have wide range of applications and can be used as biosensors in neurology, medicine, and drug delivery and chemical sensors for detecting organic vapors (Naresh & Lee, 2021; Berepiki et al., 2020). In addition, they possess high values of surface area and can be effectively used as absorbents, adsorbents, and membrane modification material, in wastewater treatment. Furthermore, they are highly efficient in abating toxic metal ions and organics/oils from polluted water (Bharati et al., 2017). Over the last decade, researchers and scientists have explored the potential of carbon nanotubes in oil–water separation owing to their relatively

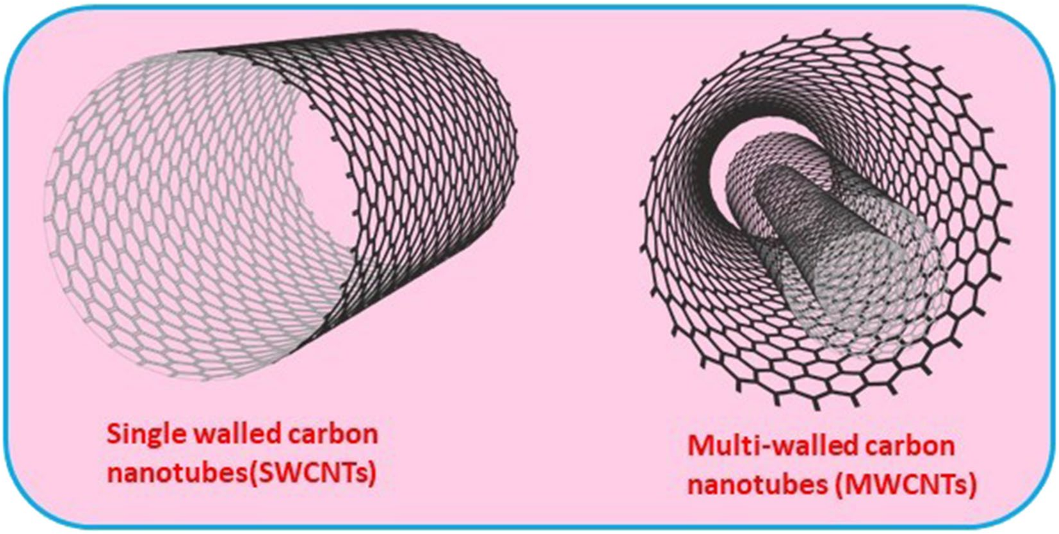

Fig. 4 Schematic illustration of single walled and multiwalled carbon nanotubes

lower surface energy, high porosity and surface area, and excellent hydrophobicity (Ye, Wang, et al., 2020). The oil–water separation performance parameters and reusability of carbon nanotube–based materials are given in Table 2.

Paul and colleagues developed membranes in which carbon nanotubes were immobilized on polytetrafluoroethylene (PTFE) micro-sized monoliths with pore sizes of 0.1 μm and 0.22 μm and were tested for separating oil–water emulsions (Paul et al., 2022). The resultant membrane was very effective in separating octane and heptane from water mixtures. The hydrophobicity was enhanced by 9%, and 16% for carbon nanotubes were immobilized on 0.1 μm and 0.22 μm PTFE monoliths. This hydrophobic nature was responsible for coalescing water molecules on the membrane surface which resulted in their serration from their oil mixtures. The water separation efficacy was greater than 99.5% for both membranes containing 0.1- and 0.22-μm PTFE monoliths and optimum carbon nanotube constituents of 3% (wt./wt.) and 6% (wt./wt.), respectively. The corresponding flux values were 44.947 Lm^{-2} h^{-1} and 54.66 Lm^{-2} h^{-1}, respectively. A hybrid membrane with hydrophobic nature was synthesized in which carbon nanotubes were grafted on carbon nanofiber membrane. The resultant membrane exhibited substantial porous framework and hydrophobic characteristics. Consequently, employing this hydrophobic membrane for separating various oil–water emulsions, the efficacy was found to be in the range between 80 and 98%. Additionally, it was highly reusable and exhibited sustained performance after 10 oil–water separation cycles. Therefore, this study provided evidence for the practical applicability of the developed hybrid membrane for oil–water separation (Liu et al., 2022). Liu and coworkers prepared a polyurethane sponge with addition of carbon nanotubes in a single step to induce simplicity and robustness with excellent hydrophobicity (Liu et al., 2021). The main aim was to analyze the effect of binding agents and binding time on the wettability of the resultant sponge. Octadecyltrichlorosilane (OTS) was chosen as an optimum binder. In addition, the extraordinary hydrophobicity was evident from water contact angle of 151.3°. Furthermore, the manufactured sponge demonstrated the ability to effectively separate organic chemicals (i.e., oils) of various densities from oil–water media. The absorptive separation capacity was approximately 15–86 times higher than the weight of the developed sponge with negligible water intake. Regarding the mechanism of the absorptive removal oil separation capability of sponge, it was noticed that the prime separation mechanisms included hydrophobic and capillary actions. Furthermore, it sustained 10 consecutive cycles of reuse with absorptive separation capability of approximately 90% of the very first absorption capacity.

The development of the state-of-the-art membranes which possess twofold functionalities such as simultaneous separation of oil and abatement of organic pollutants from oil–water emulsions is of utmost importance considering threat to human health posed by water contamination owing to increasing population and industrialization. To fulfill such requisites, a composite membrane comprising of nano-sized nickel particles and carbon nanotubes was synthesized using electroless plating technique (Rao et al., 2022). It illustrated exceptional hydrophilic and oleophobic nature. Additionally for this membrane, the water and oil contact angles were found to be 0° and 142°, respectively. On testing the oil separation capability in oil–water mixture, it displayed enhanced permeation and oil retention of 97 Lm^{-2} h^{-1} and 98.8%, respectively. Furthermore, it was very effective to catalytically abate organic contaminant (i.e., 4-nitrophenol) from polluted water. Lastly, it showed good mechanical and structural robustness even in harsh conditions such as receiving ultra-sonication.

Amidation process was utilized to fabricate a composite membrane based on polyvinyl difluoride (PVDF), diethylenetriaminepentaacetic acid, TiO_2, and multiwalled carbon nanotubes. It was evident from the images of scanning electron microscope (SEM) that diameter of the membrane fiber appreciably reduced with the inclusion of various weight percentages of based on diethylenetriaminepentaacetic acid, TiO_2, and multiwalled carbon nanotubes (Venkatesh et al., 2021). The manufactured membrane was very effective in the separation of oil from oil–water matrices owing to its great hydrophilicity and oleophobicity which were evident from complete water wettability and oil contact angle of 140°. Results displayed that oil separation efficiency from various oil–water mixtures including engine oil–water, cooking oil–water, and hexane–water was greater than 97%. Furthermore, this membrane was practically suitable for longer terms by exhibiting extraordinary

Table 2 Summary of separation performance (permeation flux, separation efficiency, absorption/adsorption capacity), wettability, selectivity, and reusability of carbon nanotube–based membranes for oil–water separation

Carbon nanotube–based membranes	Fabrication process	Surface area (m^2 g^{-1}) & porosity (%)	Wettability	Water permeation flux (Lm^{-2} h^{-1} bar^{-1})	Separation efficiency (%)	Absorption/adsorption capacity (g g^{-1})	Selectivity	Regeneration cycles	References
Immobilized carbon nanotubes on polytetrafluoroethylene membrane	Immobilization	-	Hydrophobicity (contact angle [a]151.3±2° & [b]132±2°)	[a]44.94 [b]54.66	[a]99.9 [b]99.0	-	Octane Heptane	-	Paul et al., (2022)
	Thiolene reaction	-	[c]Hydrophobicity (contact angle 154.4–168.6°)	[c]382.2-1656.1	>99%	-	Toluene, n-hexane, petroleum ether, hexadecane	-	Hu et al., (2022)
Carbon nanotube/carbon nanofiber hybrid membrane	Chemical vapor deposition	336.5 & -	Hydrophobicity (contact angle 140°)	15,400–32,670	80–98%	150	Edible oil, hexamethylene, xylene, dichlorobenzene, carbon tetrachloride	10	Liu et al., (2022)
Carbon nanotube/layered double hydroxide-modified polylactic acid membrane	Blending and electrospinning	-	Hydrophobicity (contact angle 114.01°)	-	-	35	Soybean oil	10	Liu et al., (2022)
Polyurethane/multiwalled carbon nanotube composite membrane	Electrospinning	- & 65	Hydrophobicity (contact angle 140°)	425.44	-	14.21–24.07	Heptane, hexane, kerosene, coconut oil, sunflower oil	10	Juraij et al., (2022)
Nickel/silver/carbon nanotubes composite membrane	Electroless nickel plating	-	Hydrophilicity (contact angle 0°)	97	98.8	-	n-Hexane	-	Rao et al., (2022)
Polyvinylidene fluoride-hexafluoropropylene-carbon nanotube	Electrospinning	-	Hydrophobicity (contact angle 157.8°)	360	99.5	-	n-Hexane, toluene, isooctane	50	Zhao et al., (2022)

Table 2 (continued)

Carbon nanotube–based membranes	Fabrication process	Surface area (m^2 g^{-1}) & porosity (%)	Wettability	Water permeation flux (Lm^{-2} h^{-1} bar^{-1})	Separation efficiency (%)	Absorption/ adsorption capacity (g g^{-1})	Selectivity	Regeneration cycles	References
Carbon nanotubes-dialdehyde microcrystalline cellulose	Vacuum filtration	-	Hydrophobicity (contact angle >150°)	300	>99.9	-	Trichloromethane, n-hexane, silicone oil, soybean oil, olive oil	5	Zhao et al., (2022)
Polyurethane sponge with carbon nanotubes and octadecylchlorosilane (binder)	Binding	-	Hydrophobicity (contact angle 151.3°)	-	-	86.53–85.62 36.81–38.68 35.00–36.79	Chloroform, crude oil, kerosene	10	Liu et al., (2021)
Membrane based on nano-sized Ni particles and carbon nanotubes	Electroless plating	-	Hydrophilicity (contact angle 0°)	97	98.8	-	n-Hexane	-	Rao et al., (2022)
Membrane based on polyvinyl difluoride, diethylenetriamine-pentaacetic acid, TiO_2, and multiwalled carbon nanotubes	Blade coating & phase inversion	134.1 &-	Hydrophilicity (contact angle 0°)	43.6 ± 7	>97	-	Engine oil, cooking oil, n-hexane	10	Venkatesh et al., (2021)
Monoliths based on polyurethane and carbon nanotubes	Thermally induced phase separation	- & 86.3	Hydrophobicity (contact angle 151°)	-	-	6.9–42.3	Olive oil, soybean oil, pump oil, CCl_4, chloroform, ethyl acetate	40	Ye, Wang, et al., (2020)
Meshes based on carbon nanotubes and stainless steel	Chemical vapor deposition	-	Hydrophilicity (contact angle 0°)	10639	99	-	Xylene, n-hexane, petroleum ether, diesel	10	Yin et al., (2021)

Table 2 (continued)

Carbon nanotube–based membranes	Fabrication process	Surface area (m^2 g^{-1}) & porosity (%)	Wettability	Water permeation flux (Lm^{-2} h^{-1} bar^{-1})	Separation efficiency (%)	Absorption/adsorption capacity (g g^{-1})	Selectivity	Regeneration cycles	References
Monolith based on cellulose acetate and carboxylated multiwalled carbon nanotubes	Phase separation	85.36 & 93.7	Hydrophobicity (contact angle 155°)	-	99.2	7.39–19.84	Gasoline, naphtha, soybean oil, cyclohexane, xylene, CCl_4	10	Zhang et al., (2021)
Carbon nanotubes modified with MnO_2	Vacuum filtration	-	Hydrophobicity (contact angle 153.7±0.5°)	5500	99.9	-	Sunflower oil, diesel, petroleum ether, hexane	10	Saththasivam et al., (2018)
Carbon nanotubes modified with polycarbonate	Phase separation	- & 90.1	Hydrophobicity (contact angle 159°)	-	-	8.06–12.62	Pump oil, soybean oil, n-hexane, gasoline, octane, and cyclohexane	10	Liu, Weifu, et al., (2018)
Multiwalled carbon nanotubes modified with Fe_3O_4 nanoparticles	Coupling	40.2 & -	-	-	93–96	-	Crude oil	5	Xu et al., (2019)

[a] Polytetrafluoroethylene (0.1 µm)

[b] Polytetrafluoroethylene (0.22 µm)

[c] For a range of organics including toluene, n-hexane, petroleum ether, and hexadecane

fouling resistance in underwater conditions. In the context of oil–water separation, there is an essential requirement of materials with good hydrophobic features, high porosity, and structural robustness. Along the same lines, it developed monoliths with highly porous 3-D structure comprising of thermoplastic polyurethane and carbon nanotubes (Ye, Zhang, et al., 2020). Thermally induced phase separation was utilized to develop these monoliths. The morphological evaluation of the monoliths exhibited that hierarchical framework with remarkable porosity was evident by uniformly dispersing 2% (w/w) carbon nanotubes within thermoplastic polyurethane. Results showed that the water contact angle and oil adsorptive removal capabilities were found to be 151° and 6.9 g g^{-1} to 42.3 g g^{-1}, respectively. Consequently, the hydrophobic feature, separation capability, and structural toughness and resilience were tremendously improved in comparison with the pristine monoliths. Additionally, the developed monoliths exhibited stability in their hydrophobic nature and separation capacity as high as approximately 99% in corrosion-prone conditions. Moreover, they displayed excellent ability of being reused multiple times and could undergo large number of consecutive separation squeezing cycles equivalent to 40 while maintaining high separation performance and mechanical integrity.

To provide an economical and simple alternate for developing materials which utilize costly chemical and lengthy procedures and in addition which possess extraordinary hydrophobic and oleophobic features along with appreciable fouling resistance properties, Yin and coworkers manufactured inorganic carbon nanotube stainless steel meshes in a simplistic single step via chemical vapor deposition technique (Yin et al., 2021). It not only displayed stunning hydrophilicity, oleophobicity, and fouling resistance but also demonstrated excellent fibrous structural network. Furthermore, it possessed high permeation flux and oil retention equivalent to 10,639 and 99%, respectively, which make then effective for treating oil from oil–water media. Moreover, it was proved to be practically functional under extreme environments such as high temperature, wide span of pH, and high salt concentrations.

A simple and eco-friendly phase separation technique was used to develop a highly porous monolith by cellulose acetate and carboxylated multiwalled carbon nanotubes (Zhang et al., 2021). The water and oil contact angles were found to be 155° and 0° which provided evidence of its remarkable hydrophobic and oleophilic properties. The porosity and surface areas were reported to be 93.7% and 85.36 m^2 g^{-1} owing to favorable intrinsic structure of 3-D fibrous framework. In addition, it showed appreciable adsorptive affinity in the range of 7.39–19.84 g g^{-1} for a variety of organic chemicals due to oleophilic characteristics. In extreme environments such as temperatures and pH in the range of −20 to 160°C and 1–14, respectively, it displayed great structural integrity and wettability and efficiency oil–water separation. Lastly, it exhibited great practicality in treating high volume of oil-polluted wastewater in continuous mode by providing effective and quick oil separation when applied using a low-cost in-house developed adsorption pump. One of the intrinsic limitations of carbon nanotubes for applying oil–water separation is compromising key performance parameters (permeation rate and thickness). Therefore, to introduce flexibility in the limitation, Saththasivam and colleagues developed tailored carbon nanotubes with 3-D configuration which were modified using MnO_2 via vacuum filtration (Saththasivam et al., 2018). The MnO_2-doped carbon nanotubes were found to be highly effective in separating oil–water mixtures. The separation efficiency and permeation flux were 99.9% and 5500 Lm^2 h^{-1} bar^{-1}, respectively. The permeation flux was approximately 10 times higher than obtained for pristine carbon nanotubes. The water contact angle was $152.3 \pm 0.5°$ which proved it to possess great hydrophobicity. This study highlighted that carbon nanotubes can be effectively modified for their utilization in oil–water separation processes without significant reduction in their thickness. Li and coworkers fabricated monolith with high porosity and excellent hydrophobicity/oleophilicity using multiwalled carbon nanotubes modified with polycarbonate via a phase separation method. It exhibited extraordinary porosity (90.1%) and remarkable hydrophobic and oleophilic nature with water and oil contact angles of 159° and 0°, respectively (Li et al., 2018). In addition, it showed the capability to abate a variety of organic species (pump oil, soybean oil, n-hexane, gasoline, octane, and cyclohexane) from oil–water mixtures via quick adsorption in an equilibrium time of 20 s and demonstrated high adsorption capacity (12.62 g g^{-1}) and great reusability up to 10 cycles without any significant change in the separation efficiency. It was recovered via facile evaporation/centrifugation. Therefore, these can be considered potential agents in separating oil–water matrices. Magnetic multiwalled carbon nanotubes were synthesized by coupling them with Fe_3O_4 nanoparticles. In addition, they were tailored with chemical moieties including amino, hydroxyl, and carbonyl groups and subsequently applied for crude oil–water mixtures. Results showed that these modified carbon nanotubes were highly efficient in demulsifying crude oil–water mixtures over a wide range of pH (2–10) with demulsification efficiency in the approximate range of 93–96% (Xu et al., 2019). The maximum efficiency was yielded at a dosage of 400 mgL^{-1}. Furthermore, they could be effectively reused after revering them by the magnet and showed great stable nature as their demulsifying efficiency sustained up to 5 cycles. The primary adsorption mechanisms involved in the demulsification process were π–π interactions and electrostatic forces between chemical moieties of nanotubes and organic species such as asphaltenes under acidic conditions. In the case of neutral pH conditions, the dominant mechanism was only π–π interlinkages. Furthermore, under basic conditions owing to the dominance of amino moieties, the electrostatic forces between chemical moieties of nanotubes and organic species (asphaltenes) were weakened. The results provided evidence of the practical nature of magnetic carbon nanotubes for demulsifying crude oil–water mixtures. In case of carbon nanotube–based membranes, the hydrophobic water contact angles were in the range of 114–168.8°, possessing oil–water separating efficiencies between 80% and >99%. Also, the permeation flux of carbon nanotube–based membranes was found to be in wide range between 44.94 and 32,670 Lm^{-2} h^{-1} bar^{-1}. The maximum contact angle was 168.6°, found for siloxane modified polystyrene membrane comprising of zinc oxide, carbon nanotube, and polyvinylidene fluoride. In comparison with other carbon nanotube–based membranes (Table 2), this higher contact angle was due to abundant chemical moieties such as $-CH_3$ and -COOH, located on the membrane's surface, which possess hydrophobic characteristics. A hybrid membrane consisting of carbon nanofibers and carbon nanotubes exhibited the highest permeation flux equivalent to 32,670 Lm^{-2} h^{-1} bar^{-1}. During the preparation of hybrid membranes, the growth of carbon nanotubes CNTs were predominant on both outside and inside surfaces of carbon nanofibers. This increased the pore size distribution as evident from high surface area of 336.5 m^2 g^{-1}, which facilitated in superior permeation flux (i.e., 32670 Lm^{-2} h^{-1} bar^{-1}). The reusability of the membrane is an important characteristic from commercial utility standpoint in addition to wettability and permeation flux. Carbon nanotube–based membrane consisting of polyvinylidene fluoride and hexafluoropropylene underwent 50 cycles of reuse without any considerable change in permeation flux and structural alterations. This could be linked to its narrow pore size distribution and high mechanical strength exhibiting a large tensile strength of approximately 6.5 MPa.

3.3 Carbon Nanofiber–Based Membranes

Carbon nanofiber is one of the carbon-based nanomaterials having extraordinary hydro-resistant features owing to widen structure and atomic level carbon composition. Among carbon-based nanomaterials, carbon nanofibers have not yet been thoroughly investigated for their utility in separating oil–water media as compared to other counter parts including graphene and/or its derivatives and carbon nanotubes (Zhang et al., 2018). The fabrication cost of carbon nanofibers is relatively cheaper than carbon containing nano-sized materials. In the case of oil–water separation, the performance features and regeneration capabilities of carbon nanofiber–based materials are presented in Table 3.

Considering oil–water separation a global challenge, a cross-stacking technique was utilized to develop a super-aligned carbon nanotube (SACNT) membrane with intrinsic non-polar characteristics with uniform and smooth structures. Three types of SACNT membranes such as SACNT-200, 300, and 400 were developed depending on the number of stacking layers (Zhao et al., 2022). Owing to hexagonal molecular arrangement of carbon nanotubes, the surficial chemical properties of the membrane were simplistic in nature and, therefore, avoided its fouling due to covalent bonds. Furthermore, it exhibited higher contact angles in the range between 80.0 and 126.5° for polar solvents (i.e., water) 18.8–20.9° obtained for non-polar ones (i.e., diiodomethane). In addition, it showed enhanced selectivity and permeation rate in comparison to commercially available membranes. Lastly, it exhibited promising results in

Table 3 Summary of separation performance (permeation flux, separation efficiency, absorption/adsorption capacity), wettability, selectivity, and reusability of carbon nanofiber–based materials

Carbon nanofiber–based membranes	Fabrication process	Surface area ($m^2 g^{-1}$) & porosity (%)	Wettability	Water permeation flux ($Lm^{-2} h^{-1} bar^{-1}$)	Separation efficiency (%)	Absorption/adsorption capacity ($g g^{-1}$)	Selectivity	Regeneration cycles	References
Non-polar super-aligned carbon nanotube	Cross-stacking	-	Water (CONTACT angle 124.9–126.5°) Formamide (contact angle 80–83.9°) Non-polar liquids (contact angle 18.8–20.9°)	5.184	>99.2	-	Formamide, diiodomethane	3	Zhang et al., (2023)
Carbon nanofiber–embedded resorcinol-formaldehyde	Chemical vapor deposition	-	Hydrophobicity (contact angle 157°)	426±20	99.7	-	Diesel	-	George & Verma (2022)
Polyacrylonitrile-TiO_2/polyvinylidene fluoride-co-hexafluoropropylene Jansus membrane	Sequential electrospinning	-	Hydrophobicity (contact angle 151±1.2°)	8904	99.94	-	Dichloromethane, trichloroethane, n-hexane, toluene, kerosene	10	Cui et al., (2022)
Composite membrane based on TiO_2 nanorods and carbon nanofibers	Electrospinning & hydrothermal	-	Hydrophilicity (contact angle 0–9°)	1108.8	>99	-	n-Hexane, petroleum ether, isooctane, hexadecane, and liquid paraffin	-	Wu et al., (2020)
Foam based on polyurethane and carbon nanofibers	Manual stirring & polymerization	-	Hydrophobicity (contact angle 109.43–114.06°)	-	-	2.56–5.25 (pure) 1.75–2.15 (mixed)	Diesel	-	Visco et al., (2021)

Table 3 (continued)

Carbon nanofiber–based membranes	Fabrication process	Surface area (m^2 g^{-1}) & porosity (%)	Wettability	Water permeation flux (Lm^{-2} h^{-1} bar^{-1})	Separation efficiency (%)	Absorption/adsorption capacity (g g^{-1})	Selectivity	Regeneration cycles	References
Elastic foam based on carbon nanofibers and polydimethylsiloxane	Coating	-	Hydrophobicity (contact angle 130–150°)	-	-	140–600%		10	Guo et al., (2021)
Composite membrane based on carbon nanofibers, polyurethane nanofibers, and polydimethylsiloxane	Electrospinning	-	Hydrophobicity (contact angle 157°)	6577.3 ± 571.4	>95	-	Dichloromethane, chloroform, n-hexane, toluene	30	Zhang et al., (2020)
Carbon nanofiber coated GO	Gas foaming and dip coating	163.2 & -	-	-	-	86-153	Methanol, ethanol, acetone, vegetable oil, paraffin oil	11	Jin et al., (2021)
Carbon nanofibers grafted polyurethane	Dip coating	276 & -	Hydrophobicity (contact angle 146±4°)	-	95-99.8	26.6 (n-hexane) 49.2 (toluene)	n-Hexane, n-heptane, toluene, xylene, petrol	30	Baig, Alghunaimi, Dossary, & Saleh (2019)
Material based on carbon nanofibers, polyurethane, and polystyrene	Vapor phase polymerization	184 & -	Hydrophobicity (contact angle 148±4°)	14400	>99	-	n-Hexane	-	Baig & Saleh (2018)
Carbon nanotubes modified with polycarbonate	Phase separation	139 & -	Hydrophobicity (contact angle 154.4±2.3°)	-	-	350–1250 (percent weight gain)	n-Hexane, n-octane, isooctane, nonane, dodecane	14	Baig, Alghunaimi, & Saleh (2019)
Metal rubber–carbon nanofiber-reinforced polydimethylsiloxane	Vacuum filtration		Hydrophobicity (contact angle 158°)	99–213	>99.8	-	gasoline, diesel, engine oil, and lubricating oil	-	Yang et al., (2020)

various applications. For instance, in treating wastewater and separating oil–water mixtures, its treating efficiency and separation efficacy were 2.3 times higher than conventional treatment and > 99.2%, respectively. Electrospinning and hydrothermal techniques were utilized to develop composite membranes comprising of hierarchical TiO_2 nanorod arrays and carbon nanofiber. They exhibited extraordinary hydrophilic and oleophobic characteristics. Additionally, they demonstrated high oil–water separation efficacy (i.e., >99%) and permeability (i.e., 1108.8 Lm^{-2} h^{-1} bar^{-1}). Such elevated efficiency might be due to highly porous surface morphology of these composite membranes (Wu et al., 2020). Furthermore, the introduction of OH moieties in TiO_2 enhanced the hydrophilic nature of the composite membranes. The addition of OH moieties not only revamped the separation efficacy but also proved to be responsible for their enhanced stable chemical nature. Moreover, these composite membranes showed remarkable resistance to corrosion, elevated temperatures, and reusability.

Polyurethane foam (PF) was employed in combination with carbon nanofibers for the separation of oil in oil–water media (Visco et al., 2021). Various amounts of carbon nanofibers, which acted as filling agent, were used with PF not only to enhance the oil separation efficacy from oil–water mixtures but also to augment the mechanical strength of the resultant composite sponges. It was reported that composite sponges possessed enhanced hydrophobic and oleophilic characteristics. Additionally, the absorptive oil selectivity of the sponges from oil–water mixture was also increased by approximately 22.85%. The optimum quantity of carbon nanofibers was reported to be approximately 1% (w/w) for consistent dispensation within the PF. Furthermore, the mechanical robustness of the resultant sponges was also improved as evidence by fatigue test with the addition of the filling agent (i.e., carbon nanofibers). After 80,000 fatigue repetitions, the load reduction in sponges with filling agent was 20% more than that the pure sponges (i.e., without filling agent). Therefore, the carbon nanofibers induced high fatigue strength and elasticity in the resultant sponges. On the other hand, high pressure will be required for the oil extraction from the modified sponges. Futuristic studies are required to investigate the optimum sponge composition with respect to high filler content and its subsequent distribution within the sponge.

A simplistic technique was utilized to synthesize an elastic foam with remarkable hydrophilicity. Highly porous carbon nanofibers were dispersed homogeneously on the matrix of the polydimethylsiloxane (PDMS) foam with a powerful adherence at the interfaces (Guo et al., 2021). The induction of carbon nanofibers improved the structural strength and hydrophobic nature. Additionally, the fibrous structure acted as capillaries which further improved the separation efficiency of oil from oil–water media. Furthermore, the resultant foam exhibited the ability to perform photothermal activity by absorbing light. Moreover, it possessed extraordinary resistance to corrosion and showed capability to separate various oils with wide range of densities. Owing to good photothermal performance, it readily absorbed light to significantly increase the surface temperature to as high as 75°C which aided in reducing viscosity and thus exhibited a quick and effective separation of oil on the waster surfaces.

An elastic and resilient nanofiber composite membrane possessing exceptional hydrophobicity, oleophilicity, and photothermal action was developed. It was synthesized by even dissemination of highly porous carbon nanofibers on nano-scaled polyurethane fibers (Zhang et al., 2020). It was further modified using polydimethylsiloxane (PDMS) which has good adhesive capability and strongly binds carbon nanofibers onto the nano-scaled polyurethane fibers. The coexistence of PDMS and carbon nanofibers significantly enhanced the mechanical strength without compromising its elastic nature. The tensile robustness, Young's modulus, and elasticity of the membrane increased by 21.2%, 16.4%, and 8.2%, respectively, owing to the addition of PDMS and carbon nanofibers. In context of the photothermal action, the surface temperature of the membrane speedily escalated to 90 °C in a single solar radiation. Additionally, in freezing conditions, surface temperature of the membrane increased from −32.6 to 36.6 °C. The twofold latticework of the membrane induced by carbon nanofiber and polyurethane fibers was responsible for the intake of chemical vapors in the membrane and thus exhibited excellent ability to sense chemical vapors and separate oil from oil–water mixtures. The nano-structured composite membrane showed good sensing feedback for a variety of organic vapors (dichloromethane, toluene, heptane, acetone) at concentration of 50 ppm. Additionally, for the case of dichloromethane–water mixture, the oil (dichloromethane) separation was quick as evident from high permeation of 6577.3 ± 571.4 Lm^{-2} h^{-1}. Furthermore, the membrane showed good reusability as the oil separation efficacy and permeation sustained till 30 cycles. In a recent study, Jin and colleagues synthesized a carbon nanofiber foam with multiple coatings of GO and applied it for oil–water separation (Jin et al., 2021). In fact, 2-D nano-membrane based on polyacrylonitrile/itaconic acid was transformed into a 3-D framework via gas foaming technique which was then coated with GO to yield a novel 3-D foam. The resultant foam possessed a highly integrated network and exhibited combined features of GO and carbon nanofibers (less weight, high resilience, and substantially fire resistant). Owing to the interconnected networks, these foams demonstrated high surface area which was responsible for high oil–water separation efficacy and adsorption capacities in the range between 86 g g^{-1} and 153 g g^{-1} for a variety of organic species. Furthermore, these foams demonstrated remarkable reusability and underwent 11 cycles with negligible change in adsorption capacities. Additionally, computer-based simulations related to microstructures showed enhanced surface area to volume ratio because of coating of GO on nanofiber foams.

The carbon nanofiber grafted polyurethane with exceptional hydrophobic and oleophilic features for oil–water separation has been investigated (Baig, Alghunaimi, Dossary, & Saleh, 2019). It was developed via dip coating technique. The surface area of the resultant nanomaterial was found to be 276 m^2 g^{-1} which was approximately 31-fold higher than pure polyurethane (without carbon nanofibers). Also, the corresponding pore size decreased from 2567 to 36 Å which enhanced the hydrophobic nature of the manufactured nanohybrid. Additionally, it effectively separated oil from oil–water samples. Furthermore, the oil absorptive separation capability of the fabricated nanohybrid was significantly high (i.e., 50 times greater than its own weight). Moreover, it exhibited excellent reusability. Oil was conveniently extracted by applying pressure. Also, it regained its original shape after liberating the pressure.

Baig and Saleh utilized vapor phase polymerization based on natural light to develop a highly porous framework comprising of polyurethane and carbon nanofiber-incorporated polystyrene in a reactor (Baig & Saleh, 2018). There were two prime purposes of natural light. Initially, it increased the temperature of reactor which aided in the vaporization of styrene, and secondly, it produced styrene radicals which reacted with carbon nanotubes to induce polystyrene functionalization. The surface area of the resultant material was 184 m^2 g^{-1} substantially higher than 9 m^2 g^{-1} obtained for polyurethane. Furthermore, the reinforcement of polystyrene functionalized carbon nanofibers on polyurethane increased the structural integrity and robustness. Additionally, it possessed tremendous hydrophobicity as evident from a water contact angle of 148±3°. Moreover, it effectively separated n-hexane from water under the influence of gravity without utilizing any external driving force. A novel material based on fusion of Styrofoam and carbon nanofibers was manufactured and tested it for oil–water separation. Initially, acetone treatment was performed to induce softness in Styrofoam. This treatment also aided in strong adhesion of Styrofoam with carbon nanotubes, which significantly enhanced the hydrophobic nature of the resultant material owing to micro- and macro-porosity. The induction of carbon nanotubes resulted in 3-D cavities. The results demonstrated that the resultant material possessed superb hydrophobicity/oleophilicity with water contact angle and surface area of 154.39±2.35° and 139 m^2 g^{-1}, respectively. Moreover, it efficiently separated n-hexane from oil–water mixture. This study showed that Styrofoam fused carbon nanofibers are not only eco-friendly (minimize pollution and facilitates the transformation of Styrofoam to beneficial items) but also of low cost (Baig, Alghunaimi, & Saleh, 2019).

Table 3 showed that in the case of carbon nanofiber–based membranes, the hydrophobic water contact angle, permeation flux, and separation efficiency were found to be in the range of 109.43–158°, 5.148–8904 Lm^{-2} h^{-1} bar^{-1}, and 95–99.8%, respectively. The highest contact angle was 158°, reported for Metal rubber–carbon nanofiber-reinforced polydimethylsiloxane membrane. This excellent hydrophobic nature of the membrane could be owing to intrinsic hydrophobicity of polydimethylsiloxane polymer which was coated after embedding carbon nanofiber in metal rubber. Polyacrylonitrile-TiO_2/polyvinylidene fluoride-co-hexafluoropropylene Jansus membrane exhibited the maximum value of permeation flux ~8904 Lm^{-2} h^{-1} bar^{-1} which might be due to increased pore size distribution with inclusion of 1% (wt./wt.) TiO_2 content. For commercial and practical perspective, the composite membrane based on carbon nanofibers, polyurethane nanofibers, and polydimethylsiloxane showed promising results and underwent consecutive 30 cycles of reuse without any change in permeation flux and oil–water separation efficiency. This extraordinary reusability is the consequent of its flexible nature and the strong surficial binding between the carbon nanofibers and polyurethane nanofibers. Additionally, this porous network provided various channels which resulted in high permeation flux. The generic schematic describing the oil–water separation process, hydrophobic and hydrophilic chemical functionalities, and various techniques used for the preparation and modification of GO, carbon nanotubes, carbon nanofiber–based superhydrophobic and superhydrophilic membranes is shown in Fig. 5.

4 Research Gap and Future Directions

Although a significant amount of research work has been performed in the recent years to evaluate the utilization of carbon-based membranes for the separation of oil–water mixtures, the practicality is still confined to laboratory-related investigations. Further research is an essential requirement to upscale its use in pilot or industrial applications. In this context, the critical challenges and associated future directions are listed below:

1. One of the critical parameters dictating the performance of membrane is its mechanical durability. To some extent, for the case of carbon-based membranes, the structural strength is compromised to achieve high separation efficacy owing to modifications in structure.
2. The mechanical strength can be further enhanced by utilizing modern and eco-friendly materials (i.e., self-healing synthetic and/or robust polymers) in combination with carbon-based membranes. In addition, nanoparticles with tailored chemical moieties can be co-used with carbon-based membranes to increase the structural strength without compromising the performance attributes of the membrane. The co-utilization of these advanced materials with carbon-based membranes can be achieved via various techniques using polymer grafting, interfacial assembly, and electrochemical deposition.
3. Another significant issue limiting the performance of carbon-based membranes is the accumulation of contaminants such as particulates and salts, etc., on the surface of the membrane

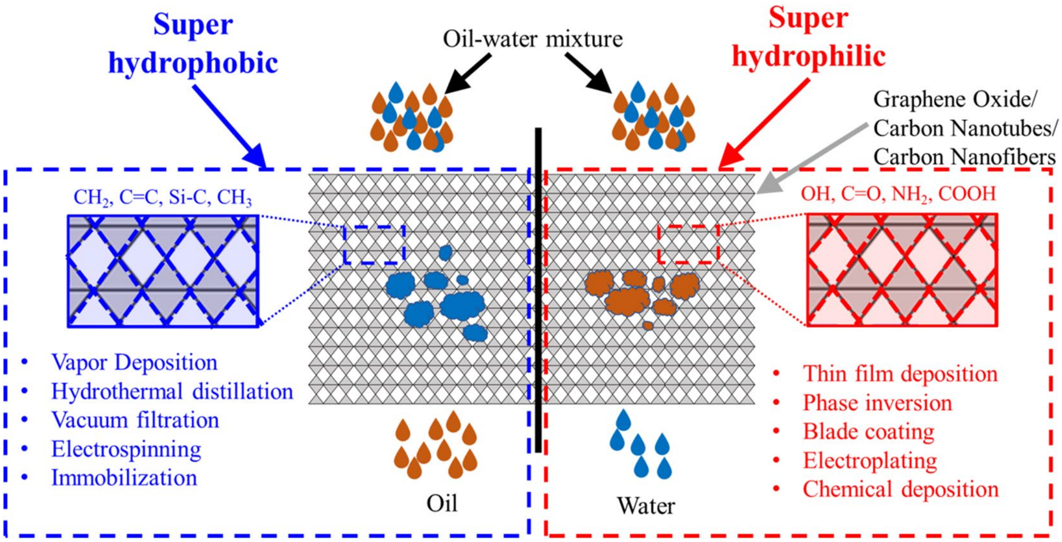

Fig. 5 A schematic of superhydrophobic and superhydrophilic membranes representing oil–water separation process, hydrophobic and hydrophilic chemical functionalities, and various techniques used for their preparation and modification

which is typically known as membrane-fouling. It appreciably reduces permeation flux and separation efficiency. Furthermore, it greatly impacts the operational span of the membrane. Integrating modern and innovative materials such as polymers or nanoparticles possessing substantial hydrophilic character (i.e., graphitic carbon nitrides, metal organic frameworks) with carbon-based membranes can augment their antifouling characteristics considering phenomenon such as hydrolysis and photocatalysis. Most of the studies have focused on the development of carbon-based membranes possessing short-term antifouling properties. Hence, persistent research is required to synthesize carbon-based membranes in combination with nanoparticles to yield composite membranes having photocatalytic ability and possessing long-term antifouling characteristics while maintaining their structural integrity. Additionally, the nanoparticles in these composite membranes can be tuned to increase their light usage efficiency by structural and morphological modifications. Furthermore, carbon-based membrane having self-cleaning features can be developed by exploiting state-of-the art zwitterions possessing excellent rejection capability. Also, the self-cleaning features can be induced in the carbon-based composite membranes by customizing their composition and structure using novel methods including electrocatalysis, energy-rich plasma technique, and 3-D printing.

4. Considering economics and large-scale application, reusability of carbon-based nanomaterials is an essential parameter. Although scientists are taking regeneration and subsequent reusability of carbon-based materials into account in their studies, still further investigations are necessary for the effective and efficient regeneration of carbon-based nano-membranes.
5. A very limited study in the literature highlighted the influence of orientation and shape on the membrane characteristics (i.e., porosity, wettability) in the context of oil–water separation. Therefore, futuristic studies should consider the evaluation of membrane orientation on its performance the separating oil–water mixtures.
6. For the case of composite carbon-based nanomaterials, less data in the literature is available regarding evaluation of optimum deposition (i.e., concentration and distribution) of nanoparticles on the respective membrane increase oil–water separation efficiency. Accordingly, studies regarding optimizing the appropriate deposition of the nanoparticles on carbon-based membranes are further required.
7. Despite sufficient literature on the development of carbon-based nanomaterials which typically used complex and delicate physical and chemical processes extended over longer periods of time (i.e., days), still literature is scant regarding one-step (fast and facile) manufacturing of carbon-based nanomaterials for the effective separation of oil–water mixtures. Thus, more scientific studies are required to develop quick fabrication processes essential from an economic point of view.
8. Influence of harsh environmental conditions (wide range of temperature, pressure, and pH pressure) on the operation and performance of carbon-based nanomaterials are relatively less explored. Therefore, considering commercial applications, further research studies are essential to synthesize carbon-based nanomaterials which possess potential to be effectively performed under a wide range of temperature, pressure, and pH.
9. The application of carbon nanotubes for filtration purposes (oil–water separation) is restricted owing to trade-off between permeation rate of the membrane and its thickness. In the literature, limited studies are available to fabricate carbon nanotube–based membranes having nano-scaled thickness to significantly enhance the permeation rate. Hence, more investigative studies are required with emphasis on the facile fabrication of nano-scaled thick carbon nanotube–based membranes to broaden their applicability for filtration systems.
10. It is evident from the literature that limited research has been performed to develop hybrid nanomaterials specifically comprising of carbon nanofibers and light-sensitive substances such as quantum dots and to further investigate their light-induced catalytic potential in the broad spectrum of water and wastewater treatment (i.e., separation of oil–water mixtures).

11. In the literature, considerable attention has been paid to test synthetic samples mimicking oil–water emulsions. However, the application of carbon-based materials to separate oil–water mixtures with wide range of viscosities and composition is limited. Hence, in this case, further investigations are deemed important.
12. Limited studies in the literature are available to simulate the structural morphology of the carbon nanofibers at molecular level using numerical and computer-assisted models in the context of oil–water separation. Thus, in this aspect, there are significant research prospects.

Owing to limitations as described above, currently, in case of carbon-based membranes, there is a huge void between the lab-scale research work and large-scale utility for commercial purposes as they are applicable to purify limited volumes of oil–water mixtures. The authors have a firm belief that this review article will facilitate the scientific community and researchers in the areas of membrane development and functionalization to perform investigations in overcoming the challenges and limitations for the successful and amplified applications of carbon-based membranes for separating oil–water mixtures.

5 Conclusions

Carbon-based membranes (membranes primarily comprising of GO, carbon nanotubes, carbon nanofibers) incorporated with versatile nanomaterials (ZnO, MnO_2, TiO_2, etc.) possess significant application in separating oil–water mixtures. In this review paper, the very recent advancements regarding their development and oil–water separation performance including separation efficiency and permeation flux have been thoroughly discussed. In case of carbon-based membranes, the hydrophobic water contact angles were ranged between 109.43 and 168.8°. The values of permeation were in a wide range between 5.148 $Lm^{-2}\ h^{-1}\ bar^{-1}$ and 32,670 $Lm^{-2}\ h^{-1}\ bar^{-1}$. Also, their respective oil–water separation efficiencies for various model emulsions such as kerosene oil, toluene, and dichloromethane were reported to be greater than 85%. They also possess excellent mechanical stability and reusability and can withstand reuse cycles in a broad range between 3 and 50. Therefore, this review underlines that carbon-based membranes make a significant contribution to effectively separate of oil–water mixtures. However, there effectiveness is still limited to laboratory-scale studies. For practical and industrial utilization, there are several challenges including development of low-cost carbon-based membranes with substantial efficiency and permeation flux, improvement in their structural stability and mechanical robustness for their extended use, single step and facile fabrication, their ability to separate limited volumes of oil–water emulsions, and their applicability to separate actual oil–water mixtures.

Acknowledgements The authors are thankful to their respective universities for providing facility of literature survey.

Data and Code Availability Not applicable

Author Contributions K.R.: conceptualization, visualization, and writing — original draft. Z.B.B., K.R., and S.M.: project administration and writing — original draft. Z.B.B., K.R., and S.M.: investigation, formal analysis, and writing — review and editing. Z.B.B., K.R., and S.M.,: writing — review and editing, formal analysis, and writing — review and editing. All authors reviewed the manuscript and approved it for publication.

Data Availability Not applicable

Declarations

Ethical Approval Not applicable

Competing Interests The authors declare no competing interests.

References

Abdalla, O., Wahab, M. A., & Abdala, A. (2020). Mixed matrix membranes containing aspartic acid functionalized graphene oxide for enhanced oil-water emulsion separation. *Journal of Environmental Chemical Engineering, 8*(5), 104269. https://doi.org/10.1016/j.jece.2020.104269

Al-Anzi, B. S., & Siang, O. C. (2017). Recent developments of carbon based nanomaterials and membranes for oily wastewater treatment. *RSC Advances, 7*(34), 20981–20994. https://doi.org/10.1039/c7ra02501g

Ali, N., Bilal, M., Khan, A., Ali, F., & Iqbal, H. M. N. (2020). Design, engineering and analytical perspectives of membrane materials with smart surfaces for efficient oil/water separation. *TrAC Trends in Analytical Chemistry, 127*, 115902. https://doi.org/10.1016/j.trac.2020.115902

Alammar, A., Park, S. H., Williams, C. J., Derby, B., & Szekely, G. (2020). Oil-in-water separation with graphene-based nanocomposite membranes for produced water treatment. *Journal of Membrane Science, 603*, 118007. https://doi.org/10.1016/j.memsci.2020.118007

Adebajo, M. O., Frost, R. L., Theo Kloprogge, J., Carmody, O., & Kokot, S. (2003). Porous materials for oil spill cleanup: A review of synthesis and absorbing properties. *Journal of Porous Materials, 10*, 159–170. https://doi.org/10.1023/A:1027484117065

An, Y.-P., Yang, J., Yang, H.-C., Ming-Bang, W., & Zhi-Kang, X. (2018). Janus membranes with charged carbon nanotube coatings for deemulsification and separation of oil-in-water emulsions. *ACS Applied Materials and Interfaces, 10*(11), 9832–9840. https://doi.org/10.1021/acsami.7b19700

Baig, N., Alghunaimi, F. I., & Saleh, T. A. (2019). Hydrophobic and oleophilic carbon nanofiber impregnated styrofoam for oil and water separation: A green technology. *Chemical Engineering Journal, 360*, 1613–1622. https://doi.org/10.1016/j.cej.2018.10.042

Baig, N., Alghunaimi, F. I., Dossary, H. S., & Saleh, T. A. (2019). Superhydrophobic and superoleophilic carbon nanofiber grafted polyurethane for oil-water separation. *Process Safety and Environmental Protection, 123*, 327–334. https://doi.org/10.1016/j.psep.2019.01.007

Baig, N., & Saleh, T. A. (2018). Initiator-free natural light-driven vapor phase synthesis of a porous network of 3D polystyrene branched carbon nanofiber grafted polyurethane for hexane /water separation. *ChemistrySelect, 3*(28), 8312–8318. https://doi.org/10.1002/slct.201801549

Baig, U., Faizan, M., & Waheed, A. (2022). A review on superwettable porous membranes and materials based on biopolymeric chitosan for oil-water separation. *Advances in Colloid and Interface Science, 303*, 102635. https://doi.org/10.1016/j.cis.2022.102635

Bastida, F., Jehmlich, N., Lima, K., Morris, B. E. L., Richnow, H. H., Hernández, T., Von Bergen, M., & García, C. (2016). The ecological and physiological responses of the microbial community from a semiarid soil to hydrocarbon contamination and its bioremediation using compost amendment. *Journal of Proteomics, 135*, 162–169. https://doi.org/10.1016/j.jprot.2015.07.023

Berepiki, A., Kent, R., Machado, L. F., & Dixon, N. (2020). Development of high-performance whole cell biosensors aided by statistical modeling. *ACS Synthetic Biology, 9*(3), 576–589. https://doi.org/10.1021/acssynbio.9b00448

Bharati, R., Sundaramurthy, S., & Thakur, C. (2017). Nanomaterials and food-processing wastewater. In *Water Purification* (pp. 479–516). Elsevier Inc..

Calcagnile, P., Fragouli, D., Bayer, I. S., Anyfantis, G. C., Luigi Martiradonna, P., Cozzoli, D., Cingolani, R., & Athanassiou, A. (2012). Magnetically driven floating foams for the removal of oil contaminants from water. *ACS Nano, 6*, 5413–5419. https://doi.org/10.1021/nn3012948

Chen, P.-C., & Zhi-Kang, X. (2013). Mineral-coated polymer membranes with superhydrophilicity and underwater superoleophobicity for effective oil/water separation. *Scientific Reports, 3*, 1–6. https://doi.org/10.1038/srep02776

Cheng, X. Q., Sun, Z., Yang, X., Li, Z., Zhang, Y., Wang, P., Liang, H., Ma, J., & Shao, L. (2020). Construction of superhydrophilic hierarchical polyacrylonitrile nanofiber membranes by: In situ asymmetry engineering for unprecedently ultrafast oil-water emulsion separation. *Journal of Materials Chemistry A, 8*(33), 16933–16942. https://doi.org/10.1039/d0ta03011b

Cheng, Y., Barras, A., Shixiang, L., Wenguo, X., Szunerits, S., & Boukherroub, R. (2020). Fabrication of superhydrophobic/superoleophilic functionalized reduced graphene oxide/polydopamine/PFDT membrane for efficient oil/water separation. *Separation and Purification Technology, 236*, 116240. https://doi.org/10.1016/j.seppur.2019.116240

Choi, Y., Kim, S. S., Kim, J. H., Kang, J., Choi, E., Choi, S. E., Kim, J. P., Kwon, O., & Kim, D. W. (2020). Graphene oxide nanoribbon hydrogel: Viscoelastic behavior and use as a molecular separation membrane. *ACS Nano, 14*(9), 12195–12202. https://doi.org/10.1021/acsnano.0c05902

Cui, W., Fan, T., Li, Y., Wang, X., Liu, X., Chao Jing, L., Ramakrishna, S., & Long, Y. Z. (2022). Robust functional janus nanofibrous membranes for efficient harsh environmental air filtration and oil/water separation. *Journal of Membrane Science, 663*, 121018. https://doi.org/10.1016/j.memsci.2022.121018

Dmitrieva, E. S., Anokhina, T. S., Novitsky, E. G., Volkov, V. V., Borisov, I. L., & Volkov, A. V. (2022). Polymeric membranes for oil-water separation: A review. *Polymers, 14*(5), 980. https://doi.org/10.3390/polym14050980

Fan, Y., Wei, L., Meng, X., Zhang, W., Yang, N., Jin, Y., Wang, X., Zhao, M., & Liu, S. (2019). An unprecedented high-temperature-tolerance 2D laminar MXene membrane for ultrafast hydrogen sieving. *Journal of Membrane Science, 569*, 117–123. https://doi.org/10.1016/j.memsci.2018.10.017

Fang, W., Liu, L., Li, T., Dang, Z., Qiao, C., Jinku, X., & Wang, Y. (2016). "Electrospun N-substituted polyurethane membranes with self-healing ability for self-cleaning and oil/water separation." *Chemistry–A. European Journal, 22*(3), 878–883. https://doi.org/10.1002/chem.201504340

George, J. K., & Verma, N. (2022). Super-hydrophobic/super-oleophilic carbon nanofiber-embedded resorcinol-formaldehyde composite membrane for effective separation of water-in-oil emulsion. *Journal of Membrane Science, 654*, 120538. https://doi.org/10.1016/j.memsci.2022.120538

Guan, L.-Z., Zhao, L., Wan, Y.-J., & Tang, L.-C. (2018). Three-dimensional graphene-based polymer nanocomposites: Preparation, properties and applications. *Nanoscale, 10*(31), 14788–14811. https://doi.org/10.1039/c8nr03044h

Guerin, T. F. (2002). Heavy equipment maintenance wastes and environmental management in the mining industry. *Journal of Environmental Management, 66*(2), 185–199. https://doi.org/10.1006/jema.2002.0583

Guo, Z., Long, B., Gao, S., Luo, J., Wang, L., Huang, X., Wang, D., Xue, H., & Gao, J. (2021). Carbon nanofiber based superhydrophobic foam composite for high performance oil/water separation. *Journal of Hazardous Materials, 402*, 123838. https://doi.org/10.1016/j.jhazmat.2020.123838

Han, R., & Peiyi, W. (2019). High-performance graphene oxide nanofiltration membrane with continuous nanochannels prepared by the in situ oxidation of MXene.

Journal of Materials Chemistry A, 7(11), 6475–6481. https://doi.org/10.1039/c9ta00137a

Han, X., & Guo, Z. (2021). Graphene and its derivative composite materials with special wettability: Potential application in oil-water separation. *Carbon, 172*, 647–681. https://doi.org/10.1016/j.carbon.2020.10.060

Hu, J., Gui, L., Zhu, M., Liu, K., Chen, Y., Wang, X., & Lin, J. (2022). Smart Janus membrane for on-demand separation of oil, bacteria, dye, and metal ions from complex wastewater. *Chemical Engineering Science, 253*, 117586. https://doi.org/10.1016/j.ces.2022.117586

Jayaramulu, K., Geyer, F., Schneemann, A., Kment, Š., Otyepka, M., Zboril, R., Vollmer, D., & Fischer, R. A. (2019). Hydrophobic metal–organic frameworks. *Advanced Materials, 31*(32), 1–31. https://doi.org/10.1002/adma.201900820

Jiang, Y.-H., Zhang, Y.-Q., Gao, C., An, Q.-D., Xiao, Z.-Y., & Zhai, S.-R. (2022). Superhydrophobic aerogel membrane with integrated functions of biopolymers for efficient oil/water separation. *Separation and Purification Technology, 282*, 120138. https://doi.org/10.1016/j.seppur.2021.120138

Jin, X., Al-Qatatsheh, A., Subhani, K., & Salim, N. V. (2021). Biomimetic and flexible 3D carbon nanofiber networks with fire-resistant and high oil-sorption capabilities. *Chemical Engineering Journal, 412*, 128635. https://doi.org/10.1016/j.cej.2021.128635

Junaidi, N. F., Diana, N. H., Othman, M. Z., Shahruddin, N. H., Alias, F. M., Lau, W. J., & Ismail, A. F. (2020). Fabrication and characterization of graphene oxide–polyethersulfone (GO–PES) composite flat sheet and hollow fiber membranes for oil–water separation. *Journal of Chemical Technology and Biotechnology, 95*(5), 1308–1320. https://doi.org/10.1002/jctb.6366

Junaidi, N. F., Diana, N. H., Othman, N. S., Fuzil, M. S., Shayuti, M., Alias, N. H., Shahruddin, M. Z., Marpani, F., Lau, W. J., Ismail, A. F., & Aba, N. F. D. (2021). Recent development of graphene oxide-based membranes for oil–water separation: A review. *Separation and Purification Technology, 258*, 118000. https://doi.org/10.1016/j.seppur.2020.118000

Juraij, K., Chingakham, C., Manaf, O., Sagitha, P., Suni, V., Sajith, V., & Sujith, A. (2022). Polyurethane/multiwalled carbon nanotube electrospun composite membrane for oil/water separation. *Journal of Applied Polymer Science, 139*(19), 1–17. https://doi.org/10.1002/app.52117

Li, P., Cai, Q., Lin, W., Chen, B., & Zhang, B. (2016). Offshore oil spill response practices and emerging challenges. *Marine pollution bulletin, 110*(1), 6–27. https://doi.org/10.1016/j.marpolbul.2016.06.020

Li, Z., Wang, B., Qin, X., Wang, Y., Liu, C., Shao, Q., Wang, N., Zhang, J., Wang, Z., Shen, C., & Guo, Z. (2018). Superhydrophobic/superoleophilic polycarbonate/carbon nanotubes porous monolith for selective oil adsorption from water. *ACS Sustainable Chemistry and Engineering, 6*(11), 13747–13755. https://doi.org/10.1021/acssuschemeng.8b01637

Liu, D., Wang, S., Tao, W., & Li, Y. (2021). A robust superhydrophobic polyurethane sponge loaded with multi-walled carbon nanotubes for efficient and selective oil-water separation. *Nanomaterials, 11*(12). https://doi.org/10.3390/nano11123344

Liu, W., Xian, W., Liu, S., Cheng, X., & Zhang, C. (2022). CNT@LDH functionalized poly(lactic acid) membranes with super oil–water separation and real-time press sensing properties. *Polymer Composites, 43*(9), 6548–6559. https://doi.org/10.1002/pc.26968

Liu, Y., Yanlei, S., Guan, J., Cao, J., Zhang, R., He, M., & Jiang, Z. (2018). Asymmetric aerogel membranes with ultrafast water permeation for the separation of oil-in-water emulsion. *ACS Applied Materials and Interfaces, 10*(31), 26546–26554. https://doi.org/10.1021/acsami.8b09362

Liu, Y., Zhang, F., Zhu, W., Dong, S., Sang, Z., Yan, X., Li, S., Liang, J., & Dou, S. X. (2020). A multifunctional hierarchical porous SiO2/GO membrane for high efficiency oil/water separation and dye removal. *Carbon, 160*, 88–97. https://doi.org/10.1016/j.carbon.2020.01.002

Liu, Z., Weifu, W., Liu, Y., Qin, C., Meng, M., Jiang, Y., Qiu, J., & Peng, J. (2018). A mussel inspired highly stable graphene oxide membrane for efficient oil-in-water emulsions separation. *Separation and Purification Technology, 199*, 37–46. https://doi.org/10.1016/j.seppur.2018.01.041

Lu, Y., & Yuan, W. (2017). Superhydrophobic/superoleophilic and reinforced ethyl cellulose sponges for oil/water separation: Synergistic strategies of cross-linking, carbon nanotube composite, and nanosilica modification. *ACS Applied Materials & Interfaces, 9*(34), 29167–29176. https://doi.org/10.1021/acsami.7b09160

Ma, J., Ping, D., & Dong, X. (2017). Recent developments of graphene oxide-based membranes: A review. *Membranes, 7*(3). https://doi.org/10.3390/membranes7030052

Meng, F.-N., Zhang, M.-Q., Ding, K., Zhang, T., & Gong, Y.-K. (2018). Cell membrane mimetic PVDF microfiltration membrane with enhanced antifouling and separation performance for oil/water mixtures. *Journal of Materials Chemistry A, 6*(7), 3231–3241. https://doi.org/10.1039/c7ta10135j

Naresh, V., & Lee, N. (2021). A review on biosensors and recent development of nanostructured materials-enabled biosensors. *Sensors, 21*(4), 1109. https://doi.org/10.3390/s21041109

Noamani, S., Niroomand, S., Rastgar, M., & Sadrzadeh, M. (2019). Carbon-based polymer nanocomposite membranes for oily wastewater treatment. *Npj Clean Water, 2*(1), 1–14. https://doi.org/10.1038/s41545-019-0044-z

Othman, N. H., Fuzil, N. S., Alias, N. H., Shahruddin, M. Z., Shayuti, M. S. M., Lau, W. J., Ismail, A. F., Abidin, S. Z., Sulaiman, S., & Kusworo, T. D. (2022). Fabrication of MoS2–RGO and MoS2–ZIF-8 membranes supported on flat alumina substrate for effective oil removal. *Emergent Materials, 5*(4), 1169–1182. https://doi.org/10.1007/s42247-021-00343-x

Ou, X., Yang, X., Zheng, J., & Liu, M. (2019). Free-standing graphene oxide-chitin nanocrystal composite membrane for dye adsorption and oil/water separation. *ACS Sustainable Chemistry and Engineering, 7*(15), 13379–13390. https://doi.org/10.1021/acssuschemeng.9b02619

Pan, Y., Liu, L., Zhang, Z., Huang, S., Hao, Z., & Zhao, X. (2019). Surfaces with controllable super-wettability and applications for smart oil-water separation. *Chemical*

Engineering Journal, 378, 122178. https://doi.org/10.1016/j.cej.2019.122178

Paul, S., Bhoumick, M. C., Roy, S., & Mitra, S. (2022). Carbon nanotube enhanced membrane filtration for trace level dewatering of hydrocarbons. *Separation and Purification Technology, 292*, 121047. https://doi.org/10.1016/j.seppur.2022.121047

Qian, D., Chen, D., Li, N., Qingfeng, X., Li, H., He, J., & Jianmei, L. (2018). TiO2/sulfonated graphene oxide/Ag nanoparticle membrane: In situ separation and photodegradation of oil/water emulsions. *Journal of Membrane Science, 554*, 16–25. https://doi.org/10.1016/j.memsci.2017.12.084

Qu, R., Li, X., Zhang, W., Liu, Y., Zhai, H., Wei, Y., & Feng, L. (2020). Photothermally induced: In situ double emulsion separation by a carbon nanotube/poly(N-isopropylacrylamide) modified membrane with superwetting properties. *Journal of Materials Chemistry A, 8*(16), 7677–7686. https://doi.org/10.1039/d0ta02919j

Rao, L., You, X., Chen, B., Shen, L., Yanchao, X., Zhang, M., Hong, H., Li, R., & Lin, H. (2022). A novel composite membrane for simultaneous separation and catalytic degradation of oil/water emulsion with high performance. *Chemosphere, 288*, 132490. https://doi.org/10.1016/j.chemosphere.2021.132490

Rasouli, S., Rezaei, N., Hamedi, H., Zendehboudi, S., & Duan, X. (2021). Superhydrophobic and superoleophilic membranes for oil-water separation application: A comprehensive review. *Materials & Design, 204*, 109599. https://doi.org/10.1016/j.matdes.2021.109599

Saththasivam, J., Yiming, W., Wang, K., Jin, J., & Liu, Z. (2018). A novel architecture for carbon nanotube membranes towards fast and efficient oil/water separation. *Scientific Reports, 8*(1), 4–9. https://doi.org/10.1038/s41598-018-25788-9

Serhan, M., Sprowls, M., Jackemeyer, D., Long, M., Perez, I. D., Maret, W., Tao, N., & Forzani, E. (2019). Total iron measurement in human serum with a smartphone. *AIChE Annual Meeting, Conference Proceedings*. https://doi.org/10.1039/x0xx00000x

Singhal, A. V., George, R., Sharma, A. K., Malwal, D., & Lahiri, I. (2020). Development of superhydrophillic tannic acid-crosslinked graphene oxide membranes for efficient treatment of oil contaminated water with enhanced stability. *Heliyon, 6*(10), e05127. https://doi.org/10.1016/j.heliyon.2020.e05127

Venkatesh, K., Arthanareeswaran, G., Bose, A. C., Kumar, P. S., & Kweon, J. (2021). Diethylenetriaminepentaacetic acid-functionalized multi-walled carbon nanotubes/titanium oxide-PVDF nanofiber membrane for effective separation of oil/water emulsion. *Separation and Purification Technology, 257*, 117926. https://doi.org/10.1016/j.seppur.2020.117926

Ventikos, N. P., Vergetis, E., Psaraftis, H. N., & Triantafyllou, G. (2004). A high-level synthesis of oil spill response equipment and countermeasures. *Journal of hazardous materials, 107*(1-2), 51–58. https://doi.org/10.1016/j.jhazmat.2003.11.009

Visco, A., Quattrocchi, A., Nocita, D., Montanini, R., & Pistone, A. (2021). Polyurethane foams loaded with carbon nanofibers for oil spill recovery: Mechanical properties under fatigue conditions and selective absorption in oil/water mixtures. *Nanomaterials, 11*(3), 1–14. https://doi.org/10.3390/nano11030735

Wang, G., Miao, J., Ma, X., Lou, C.-W., Lin, J.-H., Long, Y.-Z., Ramakrishna, S., & Fan, T. (2022). Robust multifunctional RGO/MXene@PPS fibrous membrane for harsh environmental applications. *Separation and Purification Technology, 302*, 122014. https://doi.org/10.1016/j.seppur.2022.122014

Wang, Y., & Gong, X. (2017). Special oleophobic and hydrophilic surfaces: Approaches, mechanisms, and applications. *Journal of Materials Chemistry A, 5*(8), 3759–3773. https://doi.org/10.1039/C6TA10474F

Wong, T.-S., Sun, T., Feng, L., & Aizenberg, J. (2013). Interfacial materials with special wettability. *MRS Bull, 38*, 366–371. https://doi.org/10.1557/mrs.2013.99

Wu, X., Luo, Z., Lei, Y., Wen, B., & Yang, D. (2020). Hierarchical TiO2nanorod arrays/carbon nanofiber membranes for oil-in-water emulsion separation. *Industrial and Engineering Chemistry Research, 59*(48), 21097–21105. https://doi.org/10.1021/acs.iecr.0c04831

Xue, Z., Cao, Y., Liu, N., Feng, L., & Jiang, L. (2014). Special wettable materials for oil/water separation. *Journal of Materials Chemistry A, 2*(8), 2445–2460. https://doi.org/10.1039/c3ta13397d

Xiao, X., Zongxue, Y., Yang, Z., Wang, J., & Zhu, Q. X. X. (2022). Application of in-situ microbubble method on SEP@MnO2/RGO composite membrane for efficient and long-acting treatment of oil field wastewater. *Diamond and Related Materials, 130*, 109499. https://doi.org/10.1016/j.diamond.2022.109499

Xie, W., Chen, M., Wei, S., Huang, Z., & Li, Z. (2022). Lignin nanoparticles-intercalated reduced graphene oxide/glass fiber composite membranes for highly efficient oil-in-water emulsions separation in harsh environment. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 648*, 129190. https://doi.org/10.1016/j.colsurfa.2022.129190

Xu, H., Jia, W., Ren, S., & Wang, J. (2019). Magnetically responsive multi-wall carbon nanotubes as recyclable demulsifier for oil removal from crude oil-in-water emulsion with different PH levels. *Carbon, 145*, 229–239. https://doi.org/10.1016/j.carbon.2019.01.024

Yang, Y., Ren, Z., Zhao, S., & Guo, Z. (2020). Robust superhydrophobic composite featuring three-dimensional porous metal rubber with an embedded carbon nanofiber network for emulsion separation. *Industrial and Engineering Chemistry Research, 59*(13), 6172–6182. https://doi.org/10.1021/acs.iecr.9b07053

Ye, C., Voet, V. S. D., Folkersma, R., & Loos, K. (2021). Robust Superamphiphilic membrane with a closed-loop life cycle. *Advanced Materials, 33*(15), 1–7. https://doi.org/10.1002/adma.202008460

Ye, F., Zhang, Z., Mi, Y., Huang, Z., Yuan, H., Zhang, Z., & Luo, Y. (2020). Carbon nanotubes grafted with β-cyclodextrin by an ultrasonication method and its demulsification performance in oily wastewater. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 600*, 124939. https://doi.org/10.1016/j.colsurfa.2020.124939

Ye, S., Wang, B., Shi, Y., Wang, B., Zhang, Y., Feng, Y., Han, W., Liu, C., & Shen, C. (2020). Superhydrophobic and superelastic thermoplastic polyurethane/multiwalled carbon nanotubes porous monolith for durable oil/water separation. *Composites Communications, 21*, 100378. https://doi.org/10.1016/j.coco.2020.100378

Yin, X., He, Y., Li, H., Ma, X., Zhou, L., He, T., & Li, S. (2021). One-step in-situ fabrication of carbon nanotube/stainless steel mesh membrane with excellent anti-fouling properties for effective gravity-driven filtration of oil-in-water emulsions. *Journal of Colloid and Interface Science, 592*, 87–94. https://doi.org/10.1016/j.jcis.2021.02.043

Yu, Z., Shao, L., Li, X., Zeng, H., & Liu, Y. (2019). One-step preparation of sepiolite/graphene oxide membrane for multifunctional oil-in-water emulsions separation. *Applied Clay Science, 181*, 105208. https://doi.org/10.1016/j.clay.2019.105208

Yue, X., Li, Z., Zhang, T., Yang, D., & Qiu, F. (2019). Design and fabrication of superwetting fiber-based membranes for oil/water separation applications. *Chemical Engineering Journal, 364*, 292–309. https://doi.org/10.1016/j.cej.2019.01.149

Zhang, N., Yang, X., Wang, Y., Qi, Y., Zhang, Y., Luo, J., Cui, P., & Jiang, W. (2022). A review on oil/water emulsion separation membrane material. *Journal of Environmental Chemical Engineering, 10*(2), 107257. https://doi.org/10.1016/j.jece.2022.107257

Zhang, P., Gong, J.-L., Zeng, G.-M., Song, B., Cao, W. C., Liu, H.-Y., Huan, S.-Y., & Peng, P. (2019). Novel 'loose' GO/MoS2 composites membranes with enhanced permeability for effective salts and dyes rejection at low pressure. *Journal of Membrane Science, 574*, 112–123. https://doi.org/10.1016/j.memsci.2018.12.046

Zhang, S., Huang, X., Wang, D., Xiao, W., Huo, L., Zhao, M., Wang, L., & Gao, J. (2020). Flexible and superhydrophobic composites with dual polymer nanofiber and carbon nanofiber network for high-performance chemical vapor sensing and oil/water separation. *ACS Applied Materials and Interfaces*. https://doi.org/10.1021/acsami.0c15110

Zhang, S., Liang, S., Gao, Y., Yang, W., & Huang, X. (2023). Nonpolar cross-stacked super-aligned carbon nanotube membrane for efficient wastewater treatment. *Frontiers of Environmental Science and Engineering, 17*(3). https://doi.org/10.1007/s11783-023-1630-3

Zhang, T., Bin, G., Qiu, F., Peng, X., Yue, X., & Yang, D. (2018). Preparation of carbon nanotubes/polyurethane hybrids as a synergistic absorbent for efficient oil/water separation. *Fibers and Polymers, 19*(10), 2195–2202. https://doi.org/10.1007/s12221-018-8399-1

Zhang, X., Wang, B., Wang, B., Feng, Y., Han, W., Liu, C., & Shen, C. (2021). Superhydrophobic cellulose acetate/multiwalled carbon nanotube monolith with fiber cluster network for selective oil/water separation. *Carbohydrate Polymers, 259*, 117750. https://doi.org/10.1016/j.carbpol.2021.117750

Zhao, X., Cheng, L., Jia, N., Wang, R., Liu, L., & Gao, C. (2020). Polyphenol-metal manipulated nanohybridization of CNT membranes with FeOOH nanorods for high-flux, antifouling and self-cleaning oil/water separation. *Journal of Membrane Science, 600*, 117857. https://doi.org/10.1016/j.memsci.2020.117857

Zhao, Y., Guo, J., Li, Y., Zhang, X., An, A. K., & Wang, Z. (2022). Superhydrophobic and superoleophilic PH-CNT membrane for emulsified oil-water separation. *Desalination, 526*, 115536. https://doi.org/10.1016/j.desal.2021.115536

Zhou, F., Wang, Y., Dai, L., Fang, X., Kai, Q., & Zhi, X. (2022). Anchoring metal organic frameworks on nanofibers via etching-assisted strategy: Toward water-in-oil emulsion separation membranes. *Separation and Purification Technology, 281*, 119812. https://doi.org/10.1016/j.seppur.2021.119812

Zhu, Q., Chu, Y., Wang, Z., Chen, N., Lin, L., Liu, F., & Pan, Q. (2013). Robust superhydrophobic polyurethane sponge as a highly reusable oil-absorption material. *Journal of Materials Chemistry A, 1*(17), 5386–5393. https://doi.org/10.1039/c3ta00125c