

Review

A Mini-Review of Enhancing Ultrafiltration Membranes (UF) for Wastewater Treatment: Performance and Stability

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Abstract: The scarcity of freshwater resources in many regions of the world has contributed to the emergence of various technologies for treating and recovering wastewater for reuse in industry, agriculture, and households. Deep wastewater treatment from oils and petroleum products is one of the difficult tasks that must be solved. Among the known technologies, UF membranes have found wide industrial application with high efficiency in removing various pollutants from wastewater. It is shown that the search for and development of highly efficient, durable, and resistant to oil pollution UF membranes for the treatment of oily wastewater is an urgent research task. The key parameters to improve the performance of UF membranes are by enhancing wettability (hydrophilicity) and the antifouling behavior of membranes. In this review, we highlight the using of ultrafiltration (UF) membranes primarily to treat oily wastewater. Various methods of polymer alterations of the UF membrane were studied to improve hydrophilicity, the ability of antifouling the membrane, and oil rejection, including polymer blending, membrane surface modification, and the mixed membrane matrix. The influence of the type and composition of the hydrophilic additives of nanoparticles (e.g., Multiwall carbon nanotubes (MWCNT), graphene oxide (GO), zinc oxide (ZnO), and titanium dioxide (TiO₂), etc.) was investigated. The review further provides an insight into the removal efficiency percent.

Keywords: UF membrane; nanoparticle additive; performance membrane; modification; oily wastewater



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1. Introduction

The sustainable utilization of water resources is the mainstay for the sustainable development of modern society and the economy. As a result of the rapid development of the economy and society, the pressure on the shortage of water resources has increased due to industrial and human activities which consequently discharge most of their pollutants into the environment as sewage, waste, accidental discharges, etc. [1,2].

Various technologies have appeared to clean and restore polluted water for industrial, agricultural, and human consumption, such as screening, pre-sedimentation, coagulation-flocculation, advanced oxidation processes (AOPs), and the filter membrane [3], as well as numerous techniques for the wastewater purification, containing conventional physical, chemical, biological, and membrane-based methods [4,5]. Advanced oxidation processes (AOPs) are an excellent technique for treating the contaminated wastewaters containing

organic pollutants. The biggest drawback of the AOP is its costs; the most significant are the operating and maintenance costs, which are relatively high compared to other techniques. Moreover, it is a complex chemistry tailored to specific pollutants, and the removal of residual peroxide may need to be considered [6]. The UF membrane has emerged in a wide range of industrial applications with high removal efficiency of pollutants of the wastewater especially oily wastewater; therefore, it is more effective than the other techniques employed such as AOPs. Membranes are prepared from inorganic materials (such as ceramics) and organic materials (such as polymers). Current research focuses on polymeric membranes owing to higher flexibility, best control of the mechanism of pore forming, required smaller spaces for installation, and inexpensive implementation compared to the brittle material of inorganic membranes [7].

One of the major challenges is permeate flux decline owing to fouling of the membrane (which is caused when the water contaminants stick to the membrane's surface or pass through its structure, thus reducing the membrane's performance) during the filtration process, which can be improved substantially by developing hydrophilic membranes; this could result in less oily contaminants adhering to the membrane surface, less membrane fouling, and improved water permeability [8,9]. Several researchers have tried to reduce the fouling phenomenon and enhance the hydrophilicity and performance of polymeric membranes by incorporating various nanoparticles additives (e.g., multiwall carbon nanotubes (MWCNT), graphene oxide (GO), magnesium oxide (MgO), zinc oxide (ZnO), and titanium dioxide (TiO₂), etc), which allows control with a higher degree on the ability to produce the required structure and reduce fouling of the membrane [4].

This article provides an overview of published research results on improving membrane properties by adding hydrophilic nanoparticles to them, as well as assessing their effect on the performance of UF membranes. In addition, the use of UF membranes for the treatment of oily wastewater is discussed in this review.

Previous reviews briefly highlight on a specific topic without expanding to study other related matters, as they had studied membrane formation, manufacturing procedures, installation techniques, or fouling membranes [8,10,11]. Therefore, this review dealt with more than one topic; it highlights the UF membranes' manufacturing by the addition types of nanoparticles, which greatly affect the performance of the membrane; the development of membrane technology such as surface modification; as well as the synthesis techniques used.

2. Polymeric Membranes

Every polymeric material has specified properties, making them suitable for the preparation of different membranes for the application of various separation processes. In the last decade, researchers have focused their studies on using the polymeric membranes for a wide range of applications due to better pore-forming control, easy-forming properties, and inexpensive implementation to that of ceramic-based membranes as well as outstanding mechanical properties, good chemical resistance, and low energy requirements [7].

The polymeric materials such as polyvinylidene fluoride (PVDF) [2,9,12–17], polyethersulfone (PES) [18–21], polysulfone (PSf) [22–25], polyvinyl chloride (PVC) [2,9,17,20,26], and polyacrylonitrile (PAN) [27–29] have been employed to fabricate UF membranes for the application of wastewater treatment. For example, Salahi et al. reported on two types of preparation polymeric membranes for the treatment of oily wastewater (outlet wastewater of the API unit), such as the PES/PVP and PAN UF membrane [18,27]. PVDF membranes were fabricated for treatment of oily wastewater as a result of its well toughness, high mechanical strength, and outstanding chemical stability [12]. Zhang et al. prepared the PVDF membrane to separate oil/water emulsions effectively [13], and Zhang et al. prepared PVDF/ZnO membranes by coated and blending ZnO nanoparticles with PVDF solution [14]. Moreover, Shi et al. fabricated a modified PVDF/TiO₂ membrane for oil/water emulsions separation [15]. Moreover, Yuan et al. fabricated PVDF-AH membranes by coating the membrane surface with hydrogel to separate oil/water emulsion and

determined its superior performance [30], whereas Ahmed et al. fabricated a PVDF-HFP membrane modified with cellulose to achieve a membrane with super hydrophilicity and efficiency in oil/water separation [16].

Polymeric membranes have disadvantages, such as disability to separate volatile compounds and the fouling phenomenon at the surface of the membrane that leads to reducing the permeation flux, especially for oily wastewater treatment [10]. In this regard, several approaches were conducted to improve hydrophilicity and antifouling membrane ability, long lifetimes, and oil rejection [31] by developed methods of polymer alterations which include (i) polymer-blending, (ii) membrane surface modification, and (iii) the mixed membrane matrix. Table 1 summarizes approaches for the polymeric membrane for oily wastewater treatment.

2.1. Polymer Blending

In the polymer-blending, several types of polymers are mixed together to produce miscible or immiscible dope solution. The blending approach was extensively utilized in polymeric membrane preparation owing to its ability to modify the properties of the membrane, and its versatility to integrate desired properties on the membrane [2]. The aim of the polymer-blending was used to enhance the final structural morphology, wettability, fouling resistance, and functionality of the membrane in order to improve water flux, antifouling properties, and the oil rejection rate [31].

In Masuelli et al.'s work, improvement of the PVDF/sulfonated polycarbonate (SPC) membrane was investigated. The blend-charged membranes were prepared by treating the polycarbonate with acetyl sulphate, then blended SPC with 5 wt% PVP and 15 wt% PVDF polymer at 50 °C. By using a film extensor, the finished mixture was cast onto the non-woven support. Membranes are then preserved in a water bath until they are needed. The different SPC/PVDF ratios and its oil rejection coefficient (R) for blend membranes are shown in Table 2. Whereas the resulting membrane had a high oil rejection efficiency (>96.63%), the fouling resistance reduced in membranes when it was prepared by using 2 to 4 wt.% SPC. The SEM microphotographs of the membranes are shown in Figure 1, which shows that SPC has a minor effect on the structure of the membrane: in the presence of SPC, the porous substructure densifies [32].

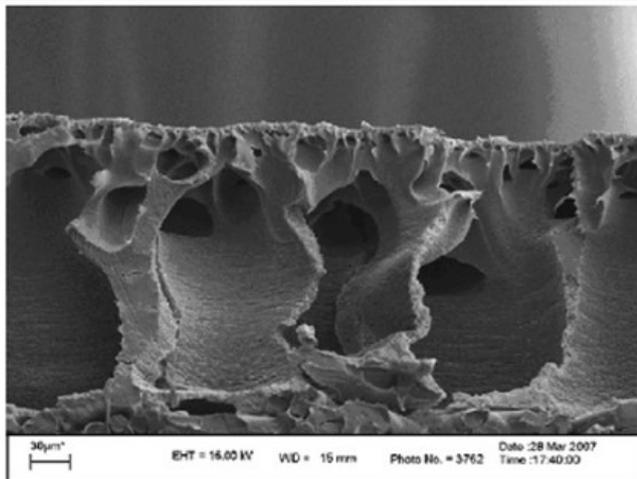
In the other study, Zhu et al. prepared superhydrophilic zwitterionic PVDF/PSH [poly (3-(N-2-methacryloxyethyl-N, N-dimethyl) ammonato propane sultone)-co-2-hydroxyethyl-methacrylate] by using non-solvent induced phase inversion (NIPS). A copolymer poly (dimethylaminoethyl methacrylate-co-2-hydroxyethyl methacrylate) (PDH) was created as a zwitterionic polymer precursor and employed as an additive in membrane preparation to make this zwitterionic PVDF membrane. PVDF and PDH were blended in n-methyl-2-pyrrolidone (NMP). The former and the latter have fluxes of 3850 and 6350 L/m² h, respectively. The blending membrane PVDF/PSH showed super hydrophilicity and superoleophobicity due to the presence of zwitterionic sulfonate groups on the membrane layer. Furthermore, the membrane has the flux recovery of 98% [33].

Table 1. Examples of research on the polymer alterations approaches for the polymeric membrane for oily wastewater treatment.

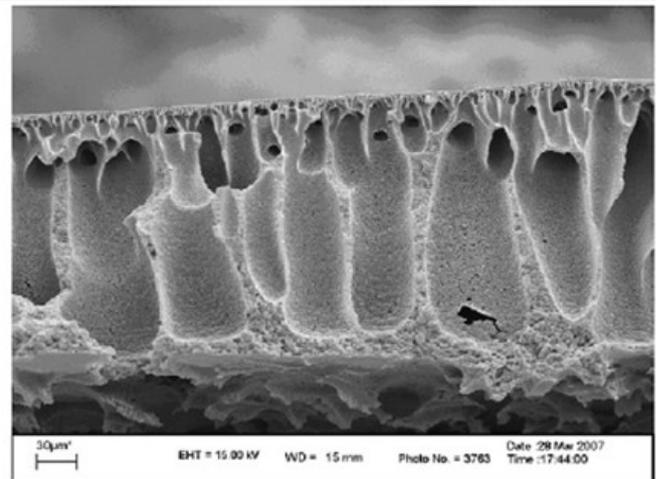
| Membrane | Fabrication Method | Properties | | | Operating Condition | Performance | | Ref. |
|---|-----------------------------|---------------|-------------|-----------------|---|-----------------|------------------|------|
| | | Pore Size, nm | Porosity, % | Contact Angle ° | | Oil Rejection % | Water Flux (LMH) | |
| PVDF/SPC | Polymer-blending | 46.06–35.89 | - | - | pressures = 20–100 kPa pH = 7 | 96.63 | - | [32] |
| PVDF/Zwitterionic Polyelectrolyte | Polymer-blending | - | - | - | - | 98.00 | 6350.00 | [33] |
| hydrophilic (PAI)-sulfonated poly (ether ether keton) | Polymer-blending | 81.00 | 79.00% | 58° | Operating time: 5 h, pressure: 400.00 kPa, temperature: 25 °C | 95.00 | - | [34] |
| PSf/PEG/PVP | Polymer-blending | 3.00–3.88 | - | - | Press. = 68.90–137.90 kPa pH = 5–8 | 90.00 | - | [22] |
| PAN | Surface modified | - | 71.7–79.6 | - | - | 85.00 | 2270.00 | [28] |
| PVDF/PVA/TiO ₂ | Surface modified (coating) | 1.95–3.68 | 83.00 | 46.05–57.07° | - | 91.50 | - | [35] |
| PNIPAAm/PPEGMA | Surface modified (grafting) | - | - | - | - | 97.00 | - | [36] |
| PVDF | Surface modified (grafting) | - | - | - | - | 98.00 | - | [37] |
| PSf/SiO ₂ | MMM | 36.21–127.20 | - | - | - | - | 17.32 | [23] |
| PVDF/LiCl-H ₂ O/SiO ₂ | MMM | 14.93–34.05 | 63.26–85.41 | - | pressure = 0.10 MPa | 62.56–98.83 | 82.50 | [38] |
| PVDF/PVP/TiO ₂ | MMM | 94.30–104.40 | 84.10–88.60 | 68.40–75.70° | Temperature: 25 °C | 99.70 | 70.48 | [39] |
| PVDF/PVP | MMM | - | - | - | - | 99.70 | 70.48 | [40] |

Table 2. The Weight percent relation SPC/PVDF and its oil rejection coefficient for the membranes. Reprinted/Adapted with permission from ref. [32]. © 2008 Elsevier B.V.

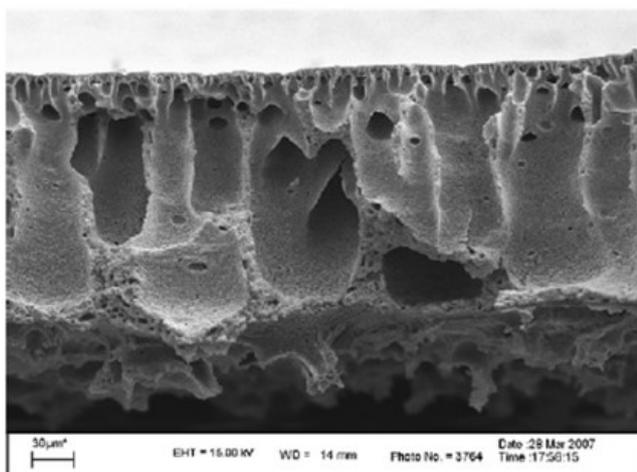
| Membrane | PVDF (%) | SPC (%) | R (%) |
|----------|----------|---------|-------|
| PVDF | 100 | - | 95.46 |
| 5-SPC | 95 | 5 | 96.66 |
| 10-SPC | 90 | 10 | 96.71 |
| 20-SPC | 80 | 20 | 96.63 |



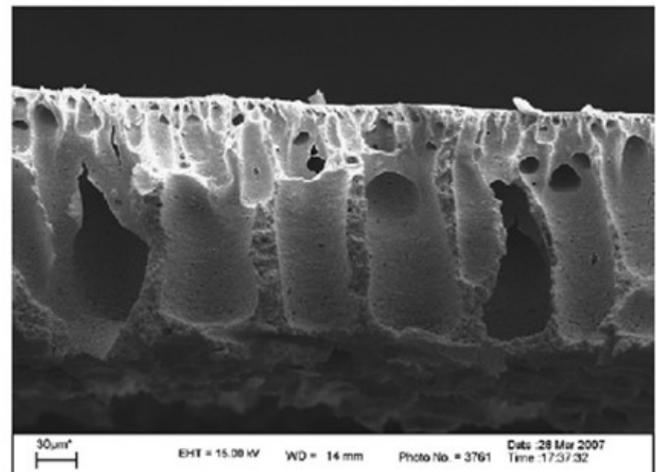
(A) PVDF Magnification 658 X



(B) 5SPC Magnification 658 X



(C) 10SPC Magnification 683 X



(D) 20SPC Magnification 657 X

Figure 1. SEM microphotographs of the Membranes. Reprinted with permission from ref. [32]. © 2008 Elsevier B.V.

Besides, polyamide imide-sulfonated poly (ether keton) (PAI-SPEEK) blend hollow fibers for oily wastewater treatment were prepared and investigated extensively by Johari et.al. [34]. Due to an excellent processability for membrane fabrication resulting from the flexible amide groups which can be an attractive amorphous thermoplastic polymer, the porosity was about 79%, the outer surface water contact angle 58° , and the mean pore size 12 nm and 81 nm for the membrane prepared by a PAI/SPEEK ratio of 85/15, respectively. The morphological structure and performance of the membrane was tested by FESEM analysis (Figure 2) and UF experiments (Figure 3). From Figure 2, it is found that the membranes have about 0.4 mm and 0.65 mm for an inner diameter and an outside

diameter, respectively. In general, the final membrane morphology is concerning with (thermodynamic and kinetic) effects of the polymer solution. Images show that the larger finger-like cavities were expanded from the outer surface into the membrane matrix by increasing the PAI/SPEEK ratio. Their results showed that the membrane was workable for the UF of oily wastewater treatment and the oil rejection over 95% [34].

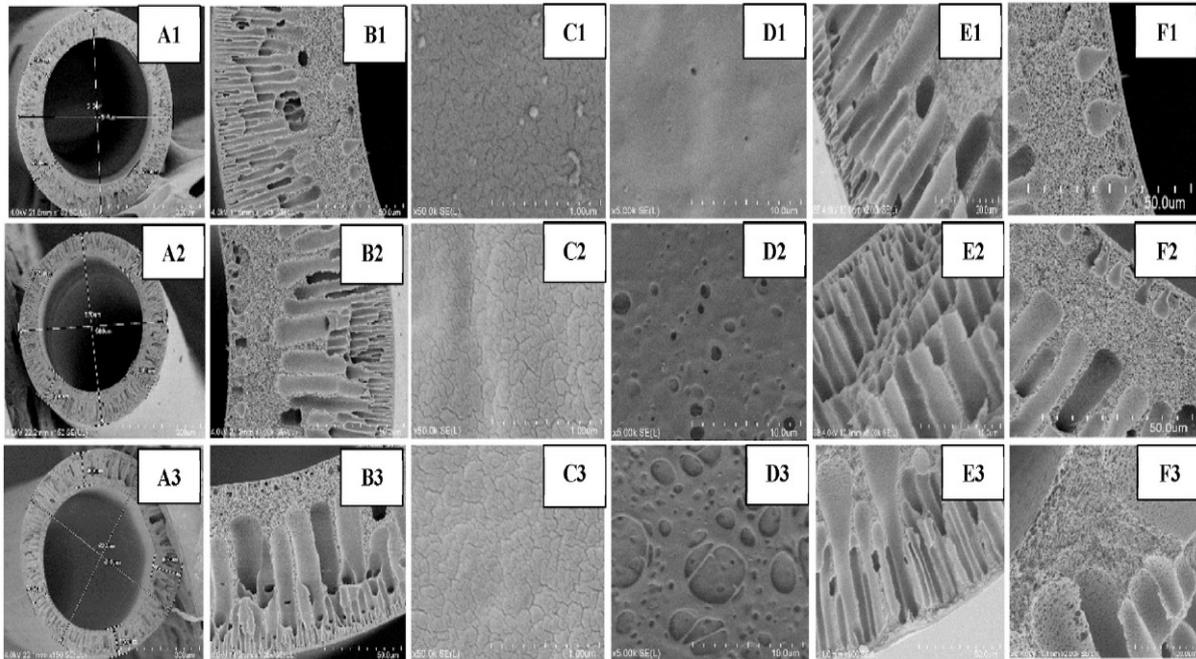


Figure 2. The FESEM images of polyamide imide-sulfonated poly (ether ether keton) (PAI-SPEEK) membranes: (1) 100/0; (2) 95/5; (3) 85/15; (A) cross-section; (B) outer-surface; (C) inner-surface; (D) outer layer; (E) inner layer; (F) inner sponge-like layer. Reprinted with permission from ref. [34]. © 2020 Elsevier Ltd.

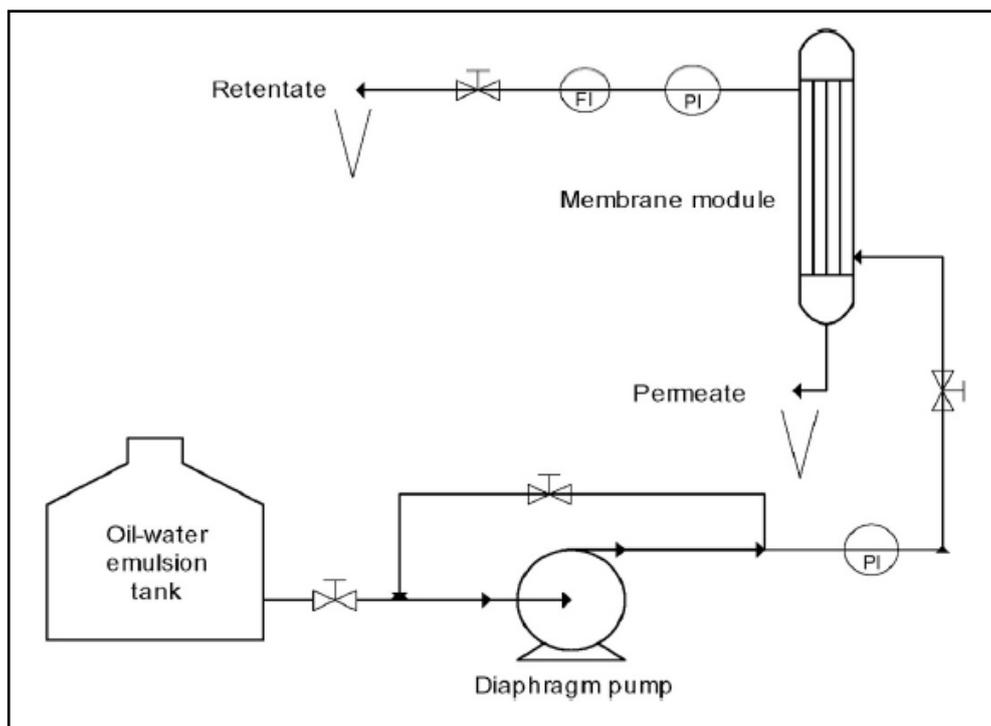


Figure 3. Schematic diagram of the experimental set-up. Reprinted with permission from ref. [34]. © 2020 Elsevier Ltd.

Moreover, similar findings were documented by Chakrabarty et al. who observed a major effect on permeate flux and the removal of oil droplet (>90%) by blend membranes composed of PSf, polyethylene glycol (PEG), and polyvinylpyrrolidone (PVP) of various molecular weights. It is noticed that the morphological membranes' properties were clearly changed by the addition of various molecular weights of PVP and PEG [22].

2.2. Surface Modified-Membranes

Recently, great interest has been focused on modifying the membranes' surface to enhance membrane performance. A significant criterion for surface modification is improved antifouling and performance which has become a main factor in membrane engineering. Surface modification of the membrane can be produced by either physical (plasma irradiation, Ion beam irradiation, and vapor phase deposition) or chemical techniques (coating, grafting, and acid base treatment) [19]. Zhang et al. used the alkali-induced phase inversion process to prepare PAN UF membranes. The NaOH is added to the coagulation bath as an additive to induce the wetting property of the PAN membrane through the alkaline-induced phase inversion process, which results in the creation of a rough structure on the membrane surface. The porosity of the PAN membranes prepared in pure water was 64.2%, while the porosity of the PAN membranes prepared in the NaOH coagulating bath was substantially higher at (71.7, 75.1, 79.6)%, corresponding to NaOH concentrations of (2, 5, 10)%, respectively. The results showed a superior recyclability and antifouling due to its ultra-low oil adherence property and permeation flux of 2270 L/m² h with an oil removal efficiency of 85% [28].

Moreover, Rajaeian et al. developed nanocomposite membranes via coating a surface modification porous of 15 wt.% PVDF support with about 2 wt.% of poly (vinylalcohol) (PVA) doped solution containing TiO₂ nanoparticles. The compositions of the casting solution of the membrane are shown in Table 3. The results showed that the oil rejection is 91.5%. The best performance was achieved in (M-3) by the embedding of 1 wt.% of carboxylated TiO₂ nanoparticles in PVA-coated PVDF membranes as shown in Figure 4, which explains schematically the effect of the carboxylated TiO₂ nanoparticles on the structure and performance of the membrane. After carboxylation, TiO₂ nanoparticles are more compatible with PVA, so an increase in the number of cross linkages between the PVA hydroxyl moieties and acid groups on the surface of TiO₂ is expected. In addition, it clarifies the well-dispersed TiO₂ nanoparticles within the PVA (M-3) vs. agglomeration of TiO₂ bonded to PVA (M-4), and a lower rejection of solutes was observed [35].

Table 3. Summary of the composition of membrane. Reprinted/Adapted with permission from ref. [35]. © 2015 Elsevier B.V.

| Membrane | PVDF (wt.%) | PVA (wt.%) | PVP (wt.%) | TiO ₂ -COOH (wt.%) | Pure TiO ₂ (wt.%) |
|----------|-------------|------------|------------|-------------------------------|------------------------------|
| PVDF | 15 | - | 2 | - | - |
| M-1 | 15 | 1 | 2 | - | - |
| M-2 | 15 | 1 | 2 | 0.5 | - |
| M-3 | 15 | 1 | 2 | 1 | - |
| M-4 | 15 | 1 | 2 | - | 1 |

Wandera et al. suggested grafting poly (N-isopropylacrylamide) (PNIPAAm)-block poly (oligo ethylene glycol methacrylate) (PPEGMA) nanolayers from the surface of the membrane to modify the surface of low molecular weight cutoff regenerated cellulose UF membranes, with the aim to prepare antifouling surfaces for produced water treatment. The modification of the membrane enhanced the TOC removal up to 97% with the reduction in the fouling rate [36]. The same surface modification technique (graft modification) was used by Masuelli et al. for treating oily wastewater by changing the charge of the PVDF membranes. Glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EDMA) were utilized as monomers in the grafting polymerization step followed by sulfonation

using sodium sulfite. The charged PVDF membranes showed about 98% of oil emulsion rejection [37].

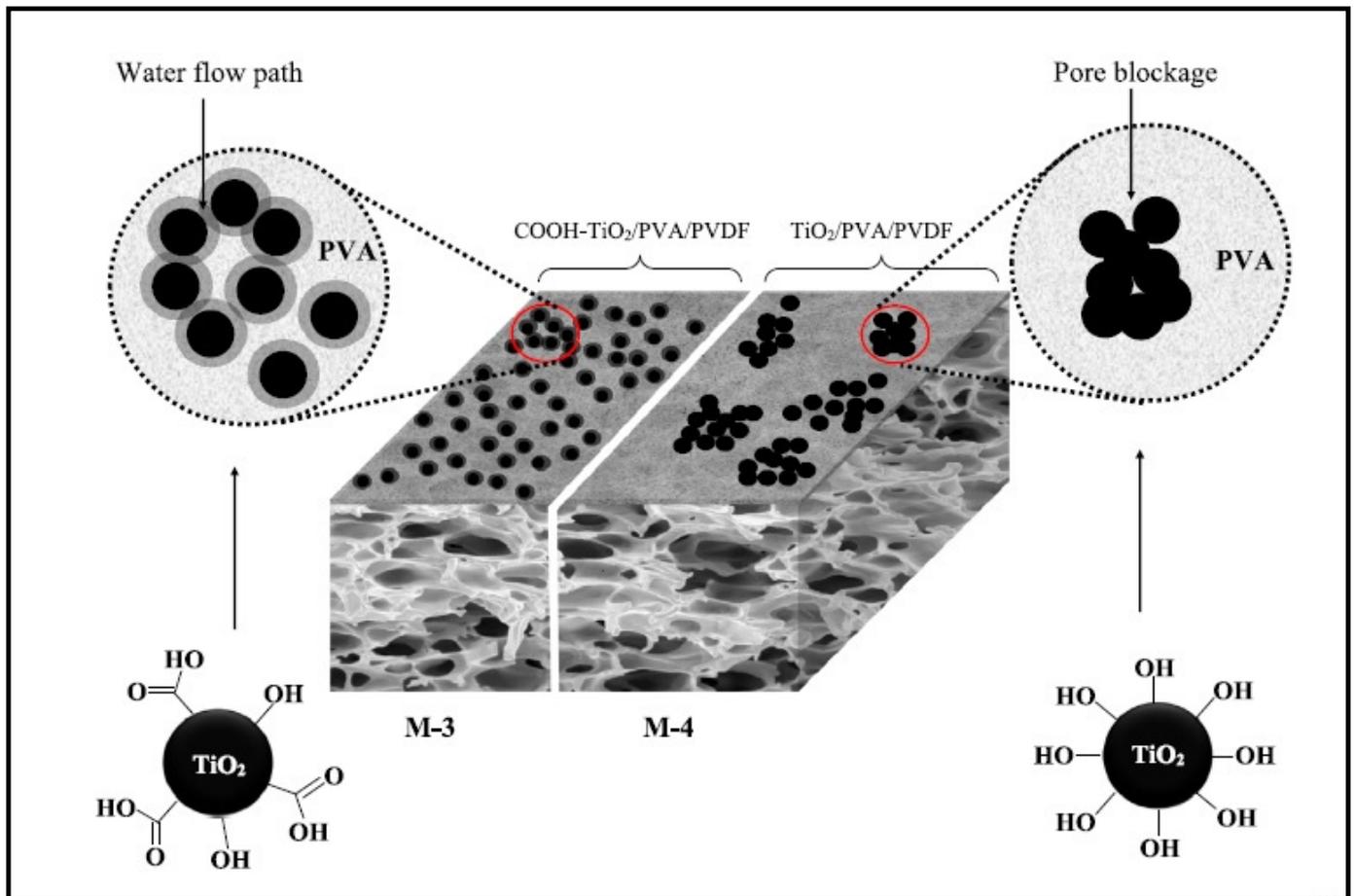


Figure 4. The dispersion of Titanium dioxide (TiO₂) nanoparticles in membrane (M-3) vs. agglomeration of TiO₂ in membrane (M-4). Reprinted with permission from ref. [35]. © 2015 Elsevier B.V.

2.3. Mixed Matrix Membranes (MMM)

A typical mixed matrix membrane MMM is fabricated by mixing an inorganic particle—such as silicon dioxide (SiO₂), carbon nanotubes (CNTs), ZnO, and TiO₂—within a matrix of the polymer. The MMM takes some of the characteristics of inorganic particles, especially their superior performance of separation. The main purpose of this mixing was to incorporate the beneficial properties of the two types of materials, thus enhancing the overall effectiveness. In the current decade, research using MMM has attracted more interest than polymer blending, as it has a greater ability to eliminate particular contaminants and the low fouling phenomenon [41].

The antifouling properties and permeability performance of the membrane were enhanced when adding SiO₂ nanoparticles into the blended composition, found by Ahmad et al. through fabricating the PSf MMM. For the modified membrane, the permeate flux (PSf-5) (17.32 L/m² h) showed 16 times an increment in membrane permeability compared to the unmodified membrane (PSf-0) (1.08 L/m² h) (Figure 5) [23].

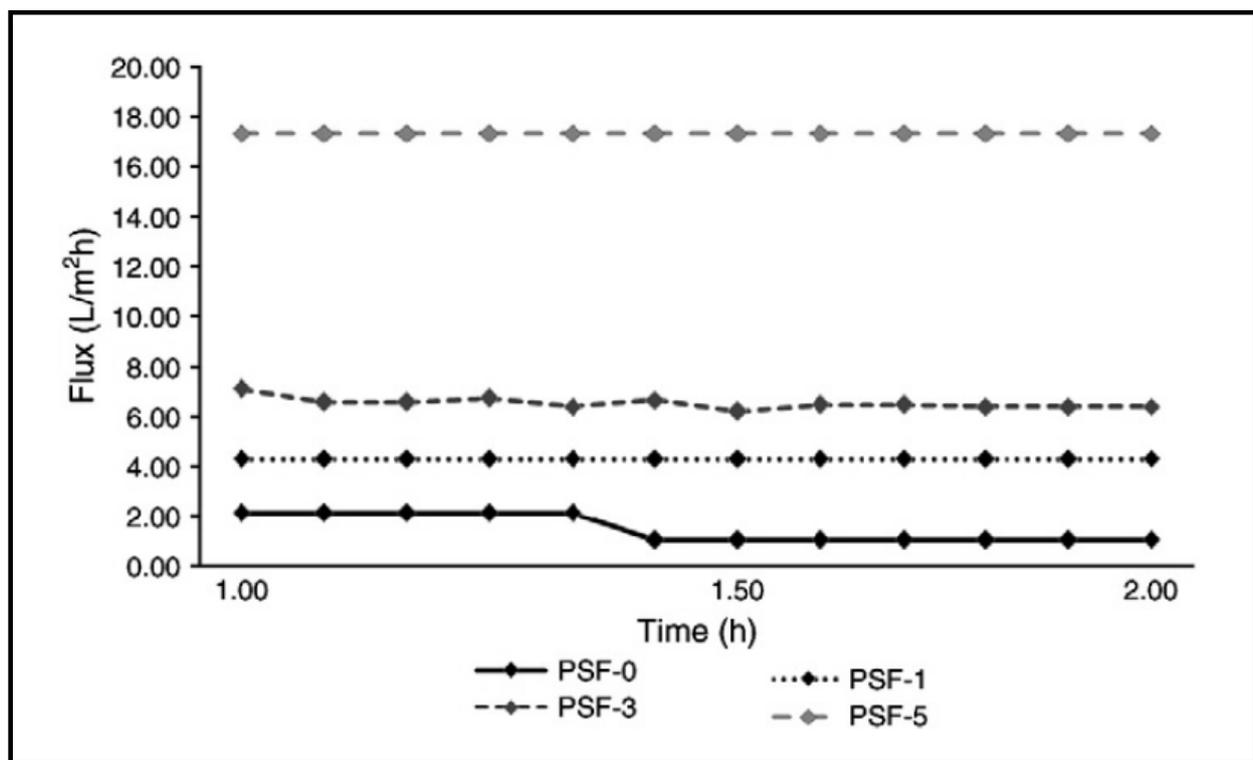


Figure 5. Permeate flux of polysulfone/silicon dioxide (PSf/SiO₂) membranes. Reprinted with permission from ref. [23]. © 2010 Elsevier B.V.

Besides, TiO₂ was also used to increase the membrane hydrophilicity in MMMs. PVDF UF membranes were fabricated by Lithium Chloride monohydrate (LiCl·H₂O) and TiO₂ nanoparticles by Yuliwati and Ismail for treating oily wastewater using MMM. At (1.95 wt.%) TiO₂, the membrane presented a maximum flux (82.5 L/m² h) and an oil removal rejection of (98.83%), respectively [38]. Similar work was also studied by Ong et al. where they discovered that at (2 wt.%) TiO₂, the PVDF-TiO₂ membrane had the highest flux [39].

Moreover, Ong et al. studied hollow fiber MMM at various concentrations of TiO₂ in the PVDF and found that with the addition of PVP, the membrane showed that the added (2 wt.%) TiO₂ concentration in the PVDF membrane played an important role in improving membrane structure by enhancing membrane hydrophilicity, pore size, and surface roughness at a (2 wt.%) TiO₂ concentration. The presence of hydrophilic PVP with TiO₂ nanoparticles had substantially improved membrane porosity. The porosity was found to be (84.10–88.60%), the water contact angle was (68.40–75.70)°, and the pore size was (94.30–104.40) nm. the PVDF-TiO₂ membrane had the water flux 70.48 L/m² h and oil rejection 99.7% [40]. In addition, Yi et al. used TiO₂/Al₂O₃ with PVDF MMM for oil/water emulsion separation. The results showed a better antifouling pattern when using modified PVDF membranes compared to the pristine PVDF membrane under the same conditions [41].

3. Membranes Structure and Performance

Membrane performance depends on its structure that is controlled through membrane synthesis methods, polymer (type and composition), and additives (type and composition). To gain the desirable performance of the membrane, many researchers investigated the effect of (i) membrane synthesis techniques, (ii) polymer selection and alterations methods, (iii) additives type and their concentration, etc. on the morphology of the membrane and thus on membrane performance.

3.1. Membranes Synthesis Techniques

Various synthesis techniques were employed to fabricate superhydrophilic surfaces of the membranes. The choice of the membrane synthesis technique is so important to improve the membrane performance with a view to modify the characteristics of the surface (i.e., roughness, hydrophilicity, biocompatibility, and functionality) to obtain the desirable membrane properties and morphologies. The most common techniques are phase inversion [8,27,28], interfacial polymerization [42,43], spray-assisted layer-by-layer [44,45], and polymer grafting [36,46]. Table 4 summarizes the most common synthesis technique of membranes.

Table 4. Examples of research on the most common synthesis technique of membranes.

| Membrane Type | Synthesis Technique | Water Flux (LMH) | Removal Efficiency % | Ref. |
|-------------------------------|-------------------------------|------------------|---|------|
| PVC/MWCNT-g-GO | phase inversion | 254.00 | COD rejection 60.00–88.90 | [9] |
| PNIPAAm)-block (PPEGMA) | polymer grafting | - | Rejection > 97.00 | [36] |
| PES/GO-SiO ₂ MMM | phase inversion | - | Oil rejection 38.00 | [20] |
| PVDF/GO@SiO ₂ /PVP | phase inversion | 1232.00 | Rejection rate 78.50 | [47] |
| PMMA–MWCNTs composites | interfacial polymerization | - | Na ₂ SO ₄ rejection > 99.00 | [42] |
| Thin-film composite PA/PVDF | interfacial polymerization | 1654.98 | - | [43] |
| CuNP-functionalized membrane | Spray-assisted layer-by-layer | - | - | [44] |
| PES/F-MWCNTs membrane | Spray-assisted layer-by-layer | - | - | [45] |
| A-MWCNTs/PVDF membrane | polymer grafting | 900.00 | Oil rejection > 99.00 | [46] |

3.1.1. Phase Inversion Technique

In the phase inversion technique or method, a de-mixing process in which at first a polymer solution with a homogeneous form is converted from a liquid phase to a solid phase in a controlled mode. This technique is commonly utilized to prepare polymeric membranes with a porous structure. In the phase inversion method, any polymer—if it is soluble in a solvent or mixture of solvents—can be utilized to fabricate a membrane. The performance and morphology of the membrane can be improved by controlling the polymer-solvent interaction through a choice of a suitable solvent [48,49].

The phase inversion technique is commonly used to prepare asymmetric polymeric membranes. Various methods are utilized to precipitate polymer solutions in the phase inversion technique, such as immersion precipitation or non-solvent induced phase inversion (NIPS), evaporation induced phase inversion (EIPS), vapor induced phase inversion (VIPS), and thermally induced phase inversion (TIPS). Due to easier preparation of NIPS, it is considered to be the most widely used technique among phase inversion techniques for preparation of polymeric membranes for the desired morphology [8,11].

Alkindy et al. fabricated a PES-based GO-SiO₂ membrane for oily wastewater treatment by the phase inversion technique, as shown in Figure 6. PES/GO-SiO₂ membrane was prepared using a loading concentration of (1.0 wt.%) of the nanoparticle to the polymer. The nanoparticle was dispersed in DMAc and ultrasonicated in a water bath for 30 min. PVP (4 wt.%) was dissolved in the solution followed by the addition of PES (16 wt.%) and stirred for 24 h at 60 °C. The dope solution was set aside for 24 h to remove trapped air bubbles (i.e., membrane degassing). The solution was subsequently cast on a polyester membrane support on clean glass at a thickness of 200 µm. The glass plate was immersed horizontally into deionized (DI) water at a temperature of 25 °C for 24 h. Finally, the

membranes were washed with DI water and stored for use. The membrane showed the highest water flux (2561 LMH) and a 38% increase in oil removal efficiency in comparison to a PES membrane [20].

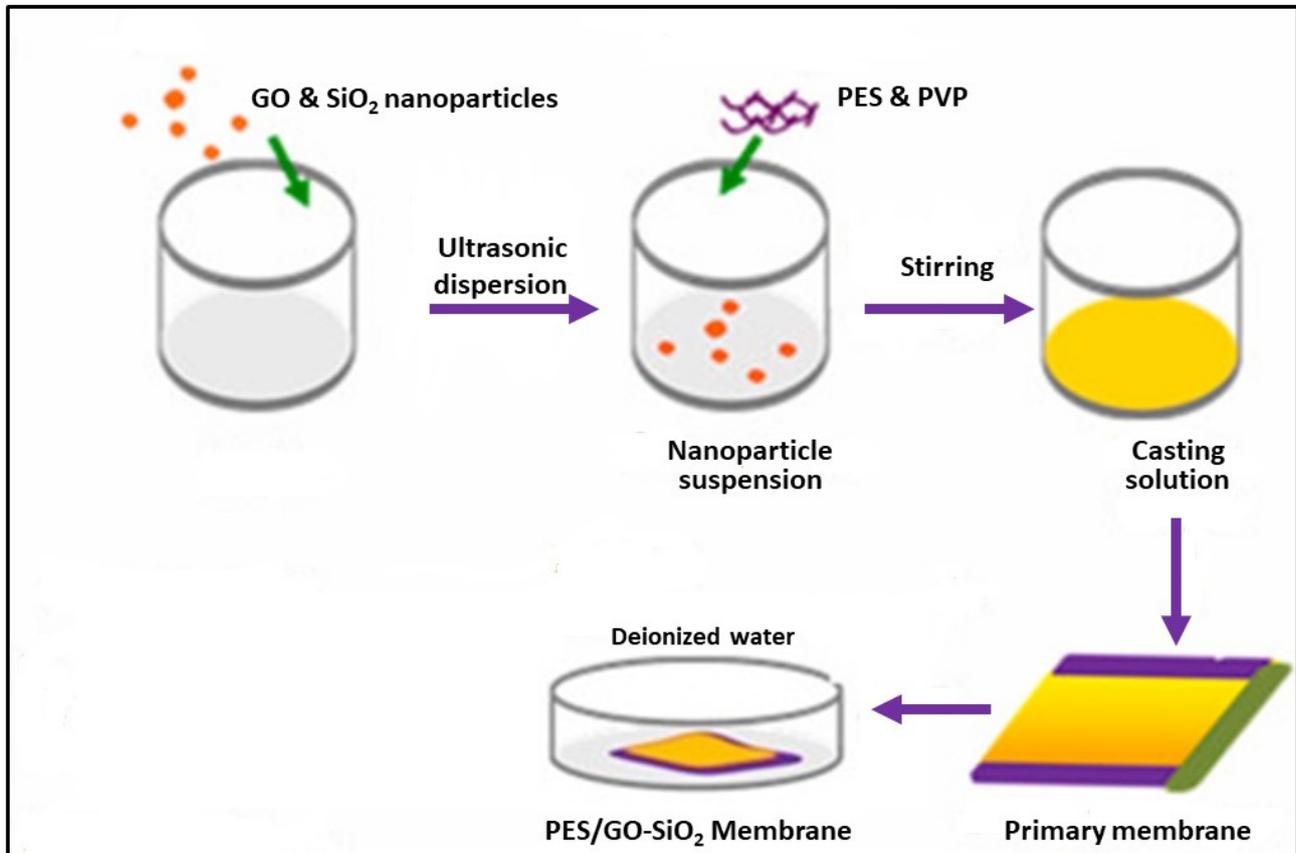


Figure 6. Schematic diagram of preparing polyethersulfone/graphene oxide-silicon dioxide (PES/GO-SiO₂) membrane using phase inversion technique.

Zhu et al. prepared novel membranes by introducing nanohybrid particles (GO/SiO₂) and polyvinylpyrrolidone (PVP) into PVDF polymer solution through the phase inversion technique. GO and SiO₂ nanoparticles were sonicated for 1 h after being applied to (0.3 wt.%) DMAC solvent. Polyvinyl pyrrolidone (PVP) powder and PVDF powder were added successively and stirred until the PVDF material had fully dissolved. The homogeneous polymer solution was permitted to fix at 60 °C for 12 h for deaeration. After extracting the bubbles, the polymer solution was cast onto a glass board. After that, the glass board was immersed horizontally in pure water at 20 °C for 24 h to extract the solvent by the coagulation bath. At the end, the membrane was washed frequently with DI water, and kept in it at 4 °C. Figure 7 shows the SEM cross sections and the AFM image of the nanohybrid membrane. The SEM cross section shows that the membrane has a composite porous structure with a skin layer and a characteristic asymmetric finger-like porous sub-layer, and the AFM image shows many serrated and conical protrusions seemingly on the surface of the PVDF/GO@SiO₂/PVP membrane, due to the difference in the roughness of the membrane which contributed to the nucleation and growth of the polymer produced by the addition of nanofillers [47].

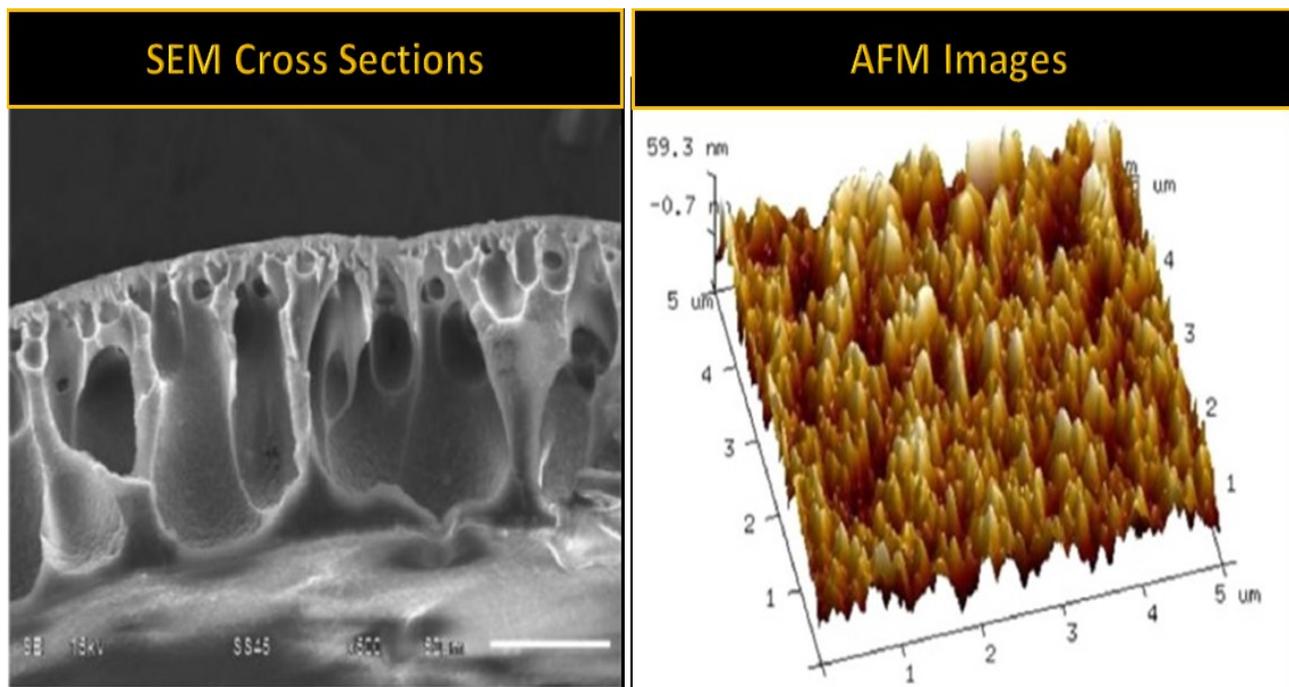


Figure 7. SEM cross sections and AFM images of the nanohybrid membrane. Reprinted with permission from ref. [47]. © 2016 Elsevier B.V.

Jalal et al. prepared a (PVC/MWCNT-g-GO) membrane by using the phase inversion method for the treatment of Al-Dura Refinery (in Baghdad, Iraq) wastewater. The dope solution was prepared by dissolving (15 wt.%) PVC in the (85 wt.%) DMAc solvent in a glass flask at a room temperature of 23 ± 1 °C. Then, the solution was left for 24 h to remove the bubbles completely. Different amounts of MWCNT-g-GO (0.0599, 0.119, and 0.219 wt.%) were separately added to the PVC solution. The composite PVC membranes were put in DI water at room temperature for precipitation. Then, it was transferred and stored in glycerol solution (40 wt.%) for 48 h to maintain the membrane structure from collapse. The water permeate flux was $254 \text{ L/m}^2 \text{ h}$ for 0.119 wt.% of MWCNT-g-GO; the membrane promoted increases in the permeation flux 66% higher than using the neat PVC ($153 \text{ L/m}^2 \text{ h}$). Due to the presence of a MWCNT-g-GO hybrid in the membrane, which changes the organization of the PVC chain packing to become disordered, resulting in better structural features, the mean pore size was (194 and 259) nm and the water contact angle (34° and 13.9°) for (0.0599 and 0.119) wt.% MWCNTS-g-GO, respectively, in the PVC solution [9].

3.1.2. Interfacial Polymerization Technique

By interfacial polymerization, Shen et al. fabricated polyamide thin-film nanocomposite (PA-TFN) membranes functionalized MWNTs grafted by poly (methyl methacrylate) (PMMA). The PA-TFN formed in a piperazine (PIP) solution by immersing PSf substrates. Then, the PMMA-MWCNTs and trimesoyl chloride (TMC) solution in toluene were poured at the PIP-soaked substrate. At ambient pressure, the PA-TFN membrane was put in an oven at 80 °C in air. Then, the TFN membranes were kept in DI water and stored at 20 °C before use, resulting in the pure water flux ($\sim 1.94 \times 10^{-3} \text{ cm}^3/\text{cm}^2 \cdot \text{s}$) through PMMA-MWCNTs (0.67 wt.%) / PA (PIP/TMC) membrane [42].

Marquez et al. prepared thin-film composite PA membranes by cosolvent-assisted interfacial polymerization on the external surface of PVDF fiber. Table 5 summarizes the interfacial polymerization conditions. Firstly, the PVDF fiber was kept in an aqueous solution containing acetone of varying concentrations and 2 wt.% monomer *m*-phenylenediamine (MPD) for 5 min. The wet PVDF was contacted to an organic phase consisting of 0.5 wt.%

TMC/toluene solution for 2 min, and then a PA layer formed immediately. Finally, the membrane was dried by air for 10 min to obtain extra polymerization; the ATR-FTIR spectra of PVDF and thin film composite PA/PVDF fiber are shown in Figure 8. The water concentration and the permeation flux were 99.88 wt.% and 1654.98 L/m² h, respectively [43].

Table 5. Summary of interfacial polymerization conditions.

| Monomer Solution | Monomer Concentration | Immersion Time | Cosolvent | Cosolvent Concentration |
|-------------------|-----------------------|----------------|-----------|-------------------------|
| Aqueous-phase MPD | 2.00 wt.% | 5 | Acetone | 0, 25, 50, 75, 100 |
| Organic-phase TMC | 0.50 wt.% | 2 | None | N/A |

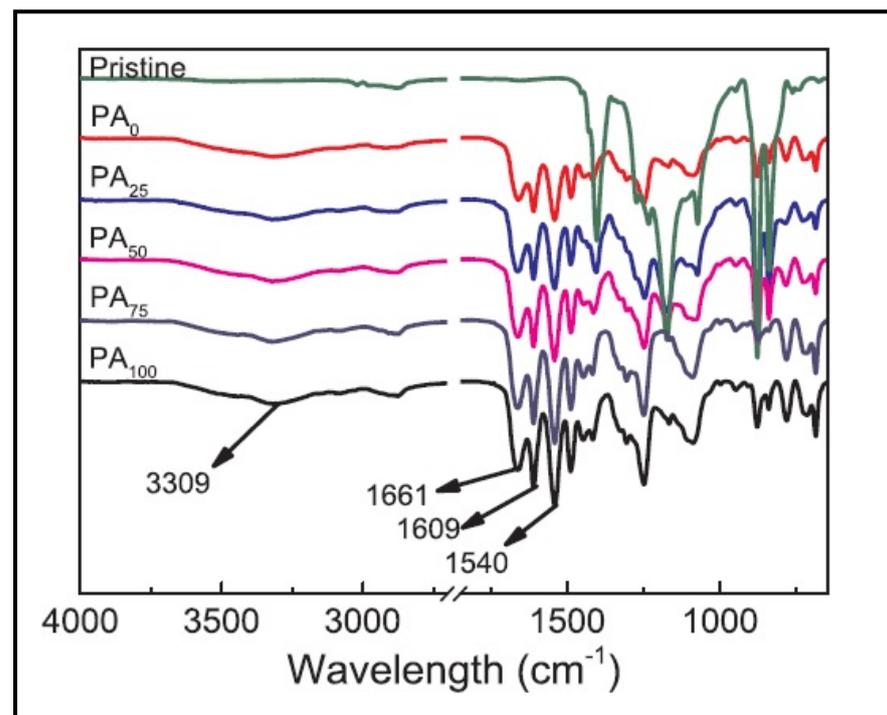


Figure 8. ATR-FTIR spectra of polyvinylidene fluoride (PVDF) and polyamide membranes by using different concentrations of acetone in aqueous phase through interfacial polymerization. Reprinted with permission from ref. [43]. © 2018 Elsevier B.V.

3.1.3. Spray-Assisted Layer-by-Layer Technique

Ma et al. established a highly efficient spray-and spin-assisted layer-by-layer (SSLbL) method for functionalizing thin film composite TFC-PA membranes with controllable copper nanoparticles CuNPs for biofouling power. A membrane coupon was adhered to a polycarbonate plate and rotated at 2000 rpm while being sprayed coated (2.1 bar). The membrane was swilled with DI water between each layer deposition and dried in the air for 10 s (with only spinning). This process completed one step of LbL deposition, resulting in a single polyethyleneimine-CuNPs/poly (acrylic) acid (PEI-CuNPs/PAA) bilayer. Multi-layer coating showed a minor impact on the water permeation flux (13.3% reduction). CuNPs could enhance the anti-biofouling property of a PA membrane and efficiently inhibit the permeate flux reduction caused by bacterial deposition on the membrane surface [44].

Liu et al. used a spray-assisted layer-by-layer technique to fabricate the PES/F-MWCNTs membrane. The F-MWCNTs were added to ethanol aqueous solution and ultrasonicated; after that, it was mixed with MWCNTs solution to form a homogeneous poly (sodium 4-styrenesulfonate) PSS solution with MWCNTs content with the aid of

another ultrasonication. The poly (diallyl-dimethylammonium chloride) (PDDA) polymer was spiked into DI water to prepare PDDA aqueous solution. The PES substrates were soaked in DI water at 25 °C for 24 h for removing the wetting agent of the membrane. The pure water flux of the bare PES membrane was reduced with more bilayer deposition of polyelectrolyte/MWCNTs [45].

3.1.4. Polymer Grafting Technique

Wandera et al. used grafting PNIPAAm-b-PPEGMA nanolayers by surface-initiated atom transfer radical polymerization (ATRP) to modify the surface of low molecular weight cutoff regenerated cellulose UF membranes, with the aim to fabricate antifouling surfaces for produced water treatment. Figure 9 shows how to use surface-initiated ATRP to modify a regenerated cellulose UF membrane with PNIPAAm-b-PPEGMA. After contacting ATRP initiator molecules with the membrane, surface-initiated ATRP was used to graft PNIPAAm chains from the initiator groups. Then, by re-starting PNIPAAm chains, PPEGMA (as the second polymer block) was grafted. The rejection was up to 97%, and the fouling rate decreased [36].

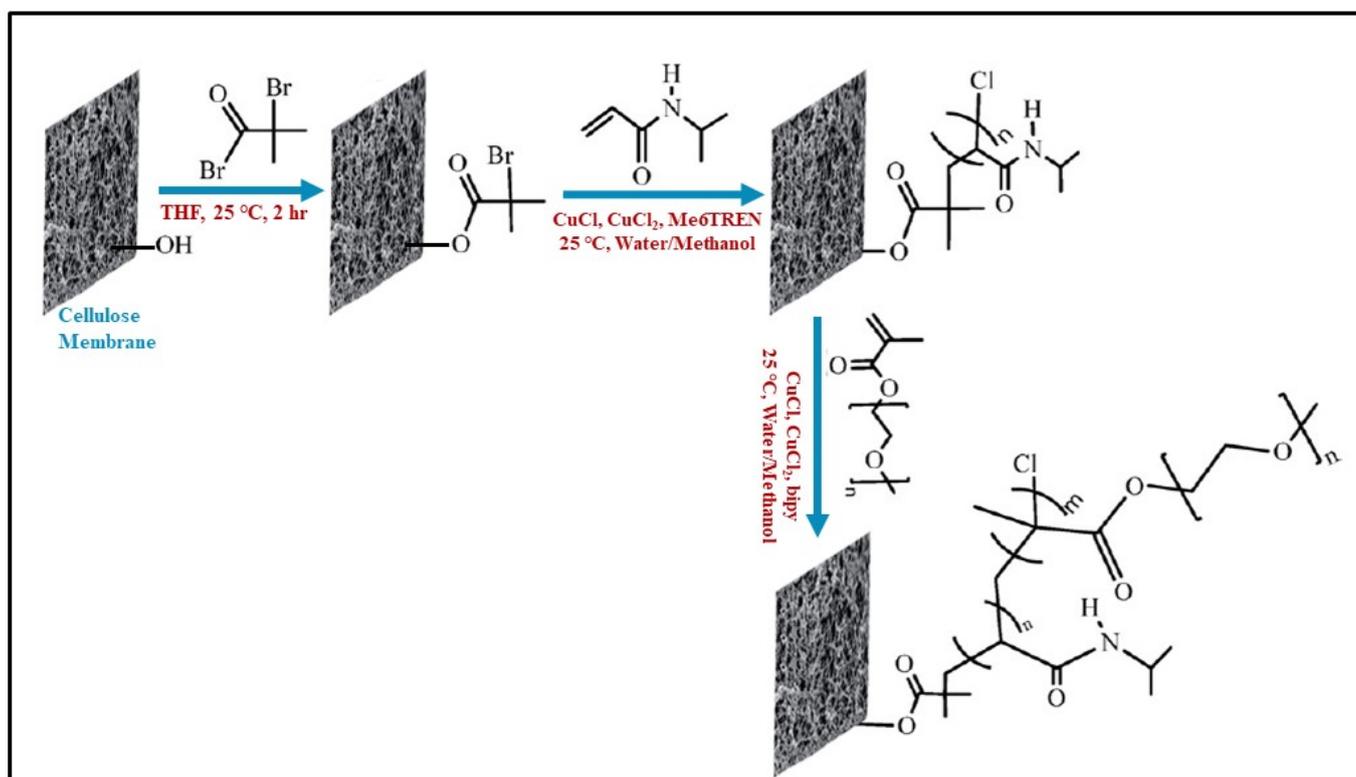


Figure 9. Schematic diagram of surface-initiated ATRP of poly (N-isopropylacrylamide) (PNIPAAm)-block-poly (oligoethylene glycol methacrylate) (PPEGMA) from cellulose Reprinted with permission from ref. [36]. © 2011 Elsevier B.V.

Yang et al. prepared DA/A-MWCNTs-treated PVDF membranes. First, they functionalized (MWCNTs) by grafting 3-aminopropyltriethoxysilane (APTES) and then decorated onto the PVDF membrane surface directly by dopamine copolymerizes. The membrane had high flux (900 L/m² h) and excellent efficiency ultra-high oil rejection (>99%). A schematic diagram of the preparation of the DA/APTES-MWCNTs decorated superhydrophilic PVDF membrane is shown in Figure 10 [46].

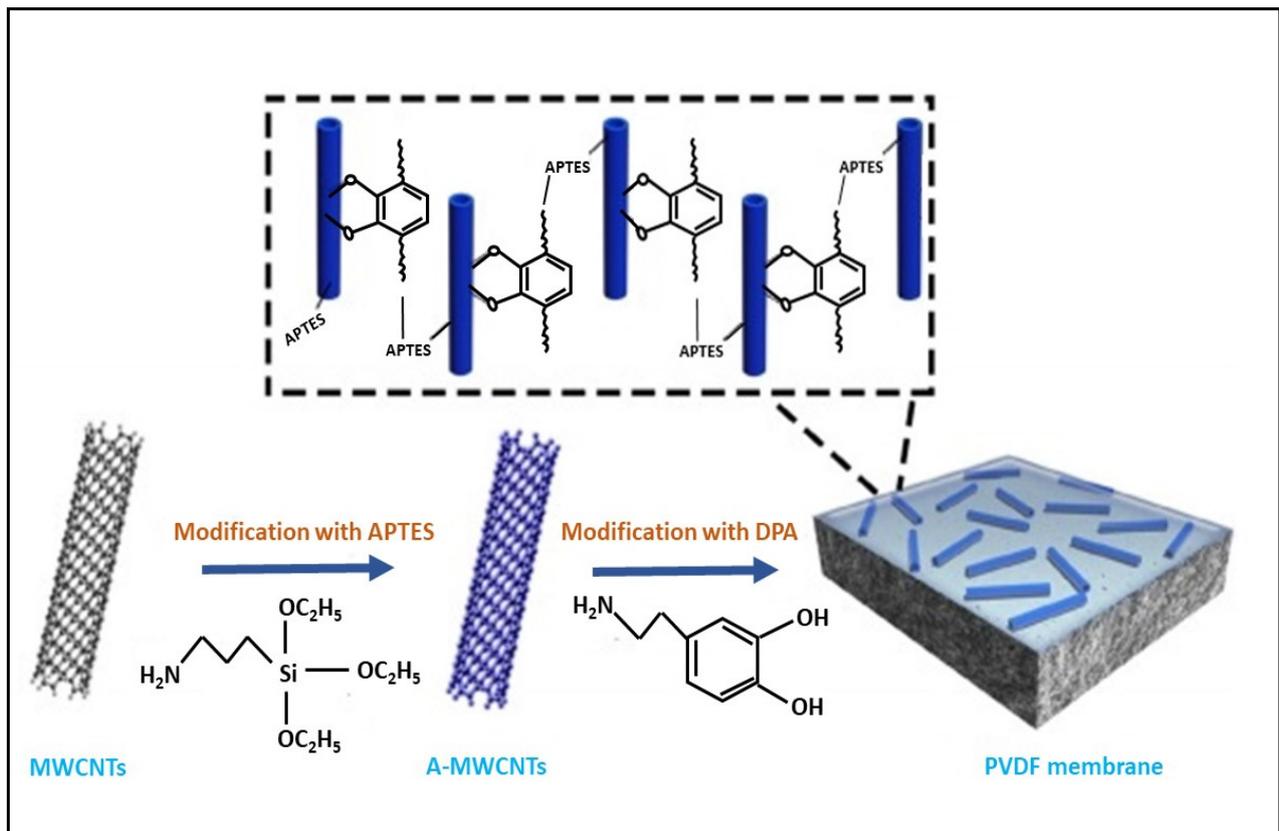


Figure 10. Schematic diagram of fabrication dopamine/3-aminopropyltriethoxysilane-multiwall carbon nanotubes (DA/APTES-MWCNTs) decorated superhydrophilic polyvinylidene fluoride PVDF membrane. Reprinted with permission from ref. [46]. © 2019 Springer Science+Business Media, LLC, part of Springer Nature.

3.2. Polymer Selection and Alterations Methods

Membrane hydrophilicity, as well as chemical, mechanical, and thermal stability of the membrane, are influenced by the polymer selection. During membrane synthesis, it plays a vital role because solvent selection depends on the polymer solubility in the solvent [8].

Various approaches, such as physical blending, chemical grafting, and surface modifications, were used in several studies to enhance membrane performance [50]. The physical blending polymer is one of these methods that has gotten a lot of attention because of the materials' comfortable operations, mild conditions, and good performances [38,51]. The effect of the polymer alterations methods on the membrane performance is described in Section 2 in detail.

3.3. Type of the Nanoparticle (NPs) Additives

Development of antifouling membranes is an intensive research area in membrane engineering. Using nanoparticles in fabricating membranes allows the ability to produce the desired structure of membranes which enhances the property of the membrane materials, and a high degree of control of the membrane fouling and permeability as well as the permeability quality [52]. Modifying the hydrophilic group on the membrane surface and creating micro-nanostructures on the surface of the membrane to increase roughness improved the membrane's hydrophilicity [53].

Nanoparticles (NPs) are classified into many groups based on their size, shape, and chemical and physical properties. Some of them are polymeric nanoparticles, carbon-based NPs, semiconductor NPs, ceramic NPs, lipid-based NPs, and metal NPs [54]. The nanoparticles that have been embedded in the matrix of the membrane are MWCNTs, halloysite nanotubes (HNTs), TiO₂, MgO, SiO₂, GO, ZnO, etc. [4]. Table 6 summarized the type of NPs and effect on the membrane performance.

Table 6. Examples of research on the type of nanoparticles (NPs) and effect on the membrane performance.

| Polymer | Method | Additive Type | Additive Conc. | Properties | | | | | Performance | Ref. |
|-------------------------------|--|----------------------|---------------------------|--------------------------|------------------------|---------------|-------------|---------------------------------|---------------------|------|
| | | | | Thickness, μm | Contact Angle $^\circ$ | Pore Size, nm | Porosity % | Rejection | | |
| PVC/MWCNT-g-GO | Phase inversion | MWCNT-g-GO | 0.06, 0.12, and 0.22 wt.% | - | 13.9–34 | 194–259 | 81.4 | COD rejection 88.9% | 254.00 at 0.12 wt.% | [9] |
| PVDF/GO@SiO ₂ /PVP | Immersion precipitation | GO@SiO ₂ | 0.30 wt.% | 100.00 | - | - | - | - | 1.23 | [47] |
| PVDF MF membrane | - | GO/TiO ₂ | GO 20.00 μg | - | 62.00–162.00 | - | - | Oil rejection 70.2% | 531.00 | [53] |
| PSf/pebax | Added | F-MWCNTs | 0.50, 1, and 2.00 wt.% | 0.75 | 42.50–55.10 | - | - | Oil rejection 98.63% at 0.5 wt% | 230.00 at 0.50% | [24] |
| PES/PDA/N-MWCNTs membranes | Coating | N-MWCNTs | 0.01 and 0.05 wt.% | - | 30.20–38.70 | 12.77 | - | Oil rejection 99% | 90.85 | [21] |
| PVDF/MWCNTs | - | MWCNTs | | 200.00 | | 20.00–60.00 | 54.02–89.36 | - | 700.00 | [55] |
| PSf hollow fiber membranes | Embedded | CNTs/GO | 1.00 wt.% | - | - | - | - | Oil rejection 98.7 \pm 1.2% | 487.90 \pm 25.40 | [25] |
| PPSU/ZnO-NPs | Phase inversion | ZnO-NPs | 0.03 wt.% | - | - | - | - | - | 76.00–107.00 | [56] |
| PVDF/SiO ₂ /GO | Thermally induced phase separation (TIPS) method | SiO ₂ @GO | 1.20 wt.% | - | 50–95 | - | - | - | 679.10 | [57] |

3.3.1. Carbon-Based Nanoparticles

CNTs are one of the most common types of carbon-based NPs. CNTs have an elongated, tubular structure and can be single named as single-walled (SWNTs), double named as double-walled (DWNTs), or many walls named as multi-walled carbon nanotubes (MWCNTs) [54]. MWCNTs were one of the strong additives with remarkable properties such as high thermal conductivity, individual mechanical property, and high specific surface area. The addition of functionalized MWCNTs allows high permeation flux due to reducing the formation boundary layers at the membrane surface and raising the membrane surface roughness [9].

As an example of the research works found in the literature that used CNTs as embedded material, Saadati and Pakizeh prepared a new PSf/pebax/F-MWCNTs nanocomposite membrane for oil/water emulsion. For enhancing the membrane characteristics, (0.5, 1, and 2) wt.% of F-MWCNT was applied to pebax solution, achieving the higher permeate flux at (0.5 wt.%) F-MWCNTs and the best oil rejection at (2 wt.%) F-MWCNTs [24]. Zarghami et al. developed a novel, fast, and facile post-functionalization of PES/PDA/N-MWCNTs membranes by utilizing amino-functionalized MWCNTs (N-MWCNTs) nanoparticle; FESEM images are shown in Figure 11. The developed membranes present high oil rejection (>99%) and flux (~1086%) compared to the undeveloped PES membrane. Moreover, evaluation of the modified membrane in cross-flow filtration produced its antifouling properties through the long-term application (16 r) [21]. Moreover, MWCNTs were used by Jalal et al. to fabricate (PVC/MWCNT-g-GO) membranes for treating refinery wastewater. The permeation flux of (0.119 wt.%) MWCNT-g-GO was 254 L/m² h, and the COD rejection increased dramatically from (60%) neat PVC to (88.9%) for both membranes made from PVC plus (0.119 or 0.219) wt.% of MWCNT-g-GO [36]. In addition, the PVDF/MWCNTs nanocomposite membrane system was developed by Moslehyani et al. The experiment was conducted by comparing neat PVDF, original PVDF/MWCNTs, and oxidized PVDF/MWCNTs (Figure 12) with water fluxes of (50, 520, and 700) L/m² h, respectively, in one hour [55].

Moreover, a nanohybrid including carboxylate CNTs/GO nanosheets was incorporated in PSf hollow fibers by Modi and Bellare to enhance the physicochemical characteristics, hydrophilicity, thermal and mechanical stability, and separation performance. The CNTs and GO nanosheets significantly affect high-water flux (487.9 ± 25.4 mL/m²/h/mmHg), greater antifouling property (flux recovery ~90.5%), and oil rejection ($98.7 \pm 1.2\%$) [25].

3.3.2. Semiconductor Nanoparticles

Semiconductor materials have properties that are similar to both metals and nonmetals, so a wide range of semiconductor NPs are extremely effective in water applications. Some examples of semiconductor nanoparticles are ZnO, ZnS, GaN, GaP, CdS, and CdSe [54].

One of the popular low-cost semiconductor NPs is ZnO; this NPs was used by Alsalhy et al. to prepare polyphenylsulfone PPSU/ZnO-NPs membranes, and they found that the hydrophilicity, mean roughness, and mean pore size were improved by increasing the ZnO-NPs concentration. The permeate flux was significantly enhanced (i.e., 76–107 L/m² h) with the addition of (0.025 wt.%) ZnO-NPs [56].

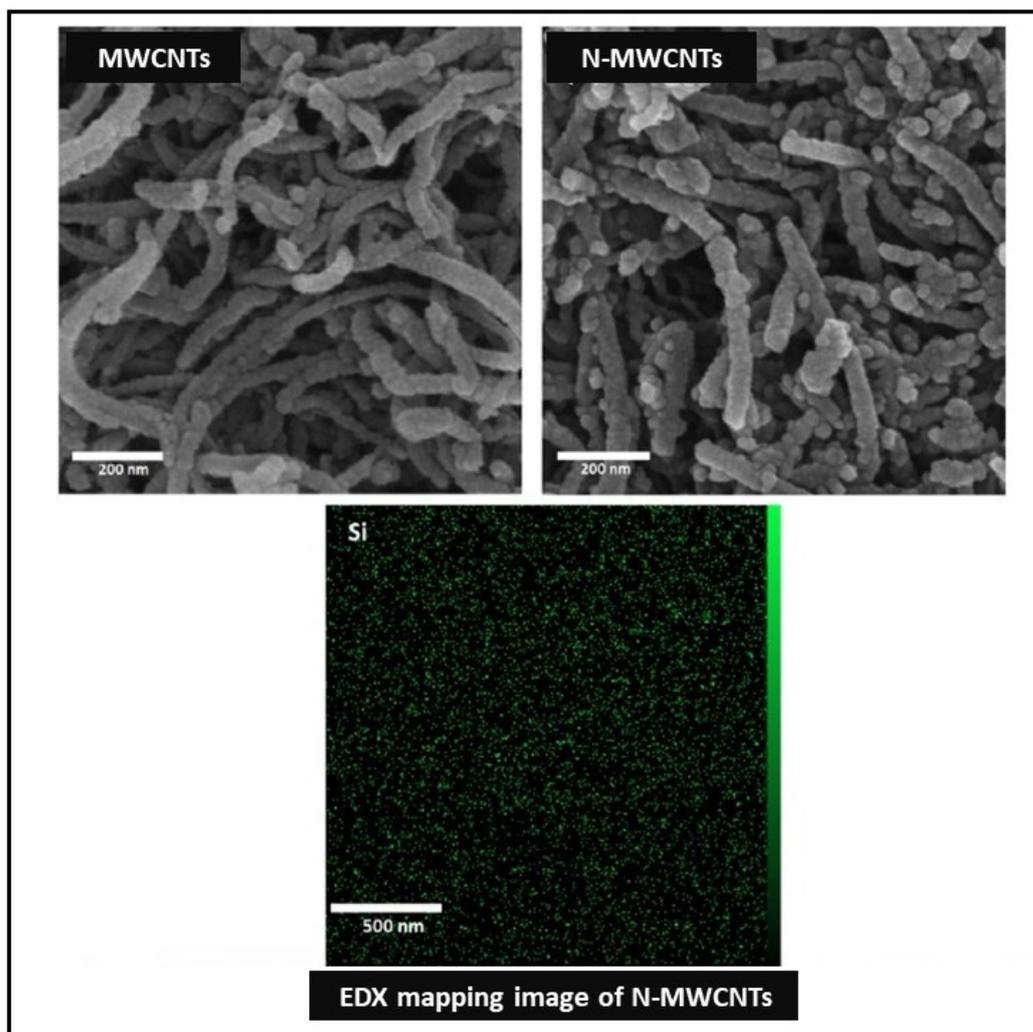


Figure 11. FESEM images of multiwall carbon nanotubes (MWCNTs) and N-MWCNTs. Reprinted with permission from ref. [21]. © 2019 Elsevier B.V.

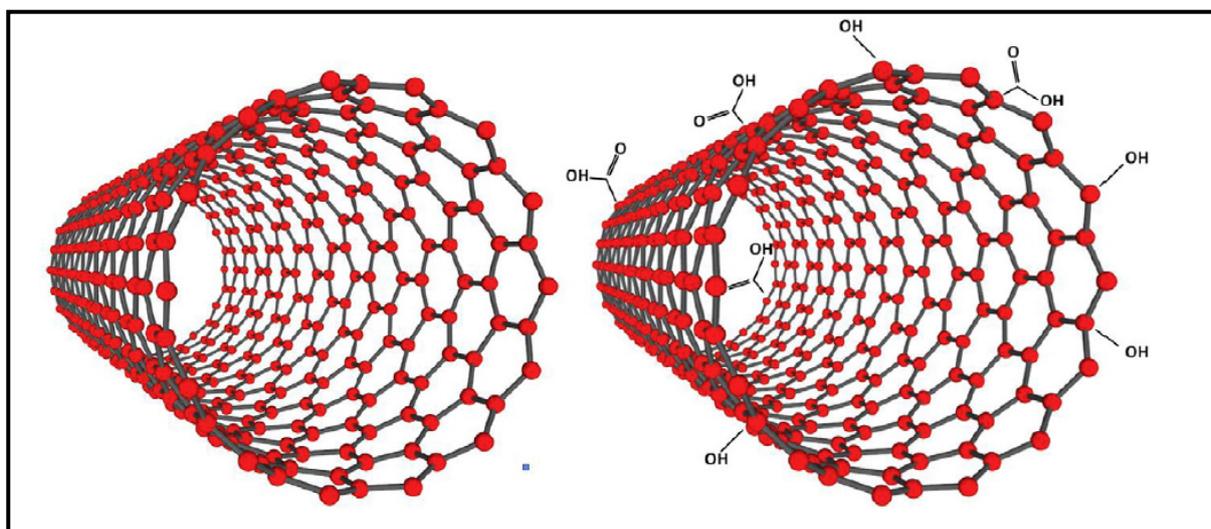


Figure 12. The oxidized multiwall carbon nanotubes (MWCNT) surface with acid mixture. Reprinted with permission from ref. [55]. © 2015 Elsevier B.V.

3.3.3. Ceramic Nanoparticles

Ceramic nanoparticles consist mostly of oxides, carbides, phosphates, and metal carbonates and metalloids such as calcium, titanium, silicon, etc. Because of their chemical inertness and high heat resistance, it is possible to use them in a wide range of applications. Some examples of ceramic NPs are silica (SiO_2), titanium oxide (TiO_2), alumina (Al_2O_3), hydroxyapatite (HA), and zirconia (ZrO_2) [54]. Several researchers utilized the ceramic NPs as an additive in polymer solution; for example, Li et al. used SiO_2 -GO to prepare a PVDF/ SiO_2 -GO nanohybrid; the TEM images of GO and SiO_2 -GO nanosheets are shown in Figure 13. The results showed that when the (0.9 wt.%) concentration of SiO_2 -GO was added in the PVDF solution, the PVDF/ SiO_2 -GO membrane (M-4) produced the lowest permeation flux ($182.6 \text{ L/m}^2 \text{ h}$) and a higher removal (91.7%). However, the over-high addition of SiO_2 /GO (1.2 wt.%) leads to the superior permeation flux ($679.1 \text{ L/m}^2 \text{ h}$) [57]. The SiO_2 /GO nanohybrid particles were also used by Zhu et al. to prepare the PVDF/GO@ SiO_2 /PVP membranes. The synthesis process, and the TEM and FESM images of nanoparticles GO@ SiO_2 , are shown in Figures 14 and 15, respectively. Figure 14 shows the synthesis process of nanoparticles GO- SiO_2 , and the C-O-Si structure was formed on the GO surface, which made it so that the nano-silica particles were firmly attached to the surface of GO, and Figure 15 shows SiO_2 particles as “black balls” and “white balls” which are dispersed homogeneously between the GO sheets. The PVDF/GO@ SiO_2 /PVP membrane had much lower adhesion forces than PVDF/PVP membranes, implying that the PVDF/GO@ SiO_2 /PVP membrane has superior performance and antifouling capabilities among nanohybrid membranes. Due to the effects of GO/ SiO_2 and PVP, the membrane had higher rejection, higher flux, and a great ability of antifouling [47].

The TiO_2 had received most attention due to its ease of preparation, stability under harsh conditions, and commercial availability. It is an ideal material for preparing a composite membrane for oil/water separation, as it can achieve excellent oleophobicity and smooth water filtration that reduce membrane fouling. Wu et al. fabricated the membrane by assembling TiO_2 nanotubes and GO nanosheets for oil/water separation, which improved the hydrophilicity, permeability, and anti-oil-fouling ability of the membranes [53].

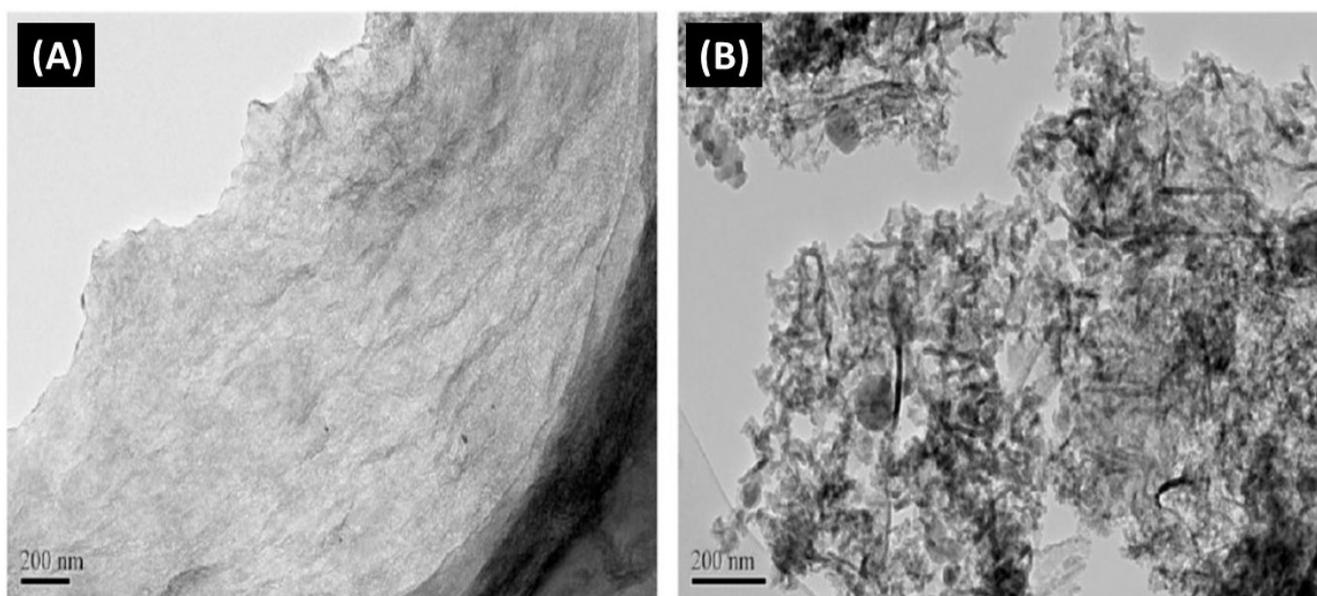


Figure 13. TEM image of (A) Graphene oxide (GO) nanosheets; (B) silicon dioxide-Graphene oxide (SiO_2 -GO) nanosheets. Reprinted with permission from ref. [57]. © 2016 Elsevier B.V.

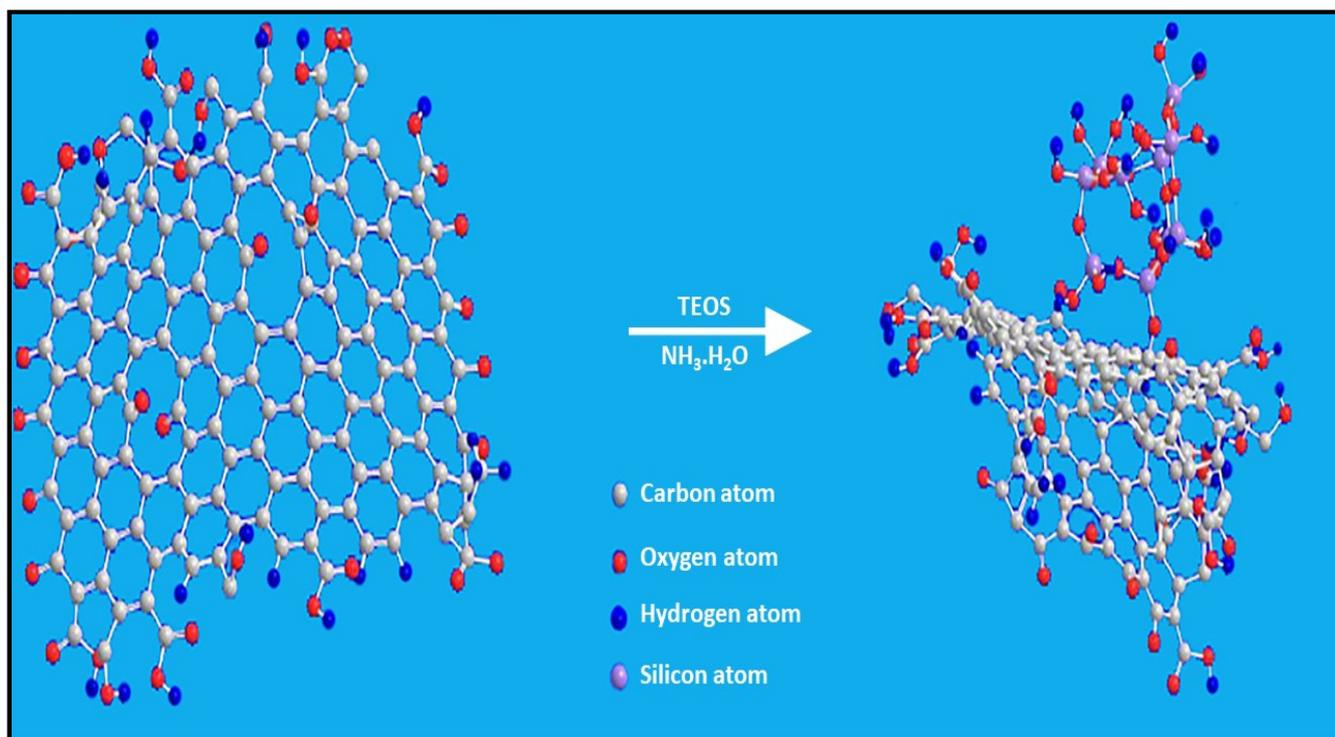


Figure 14. The synthesis process of nanoparticles silicon dioxide-Graphene oxide (GO-SiO₂). Reprinted with permission from ref. [47]. © 2016 Elsevier B.V.

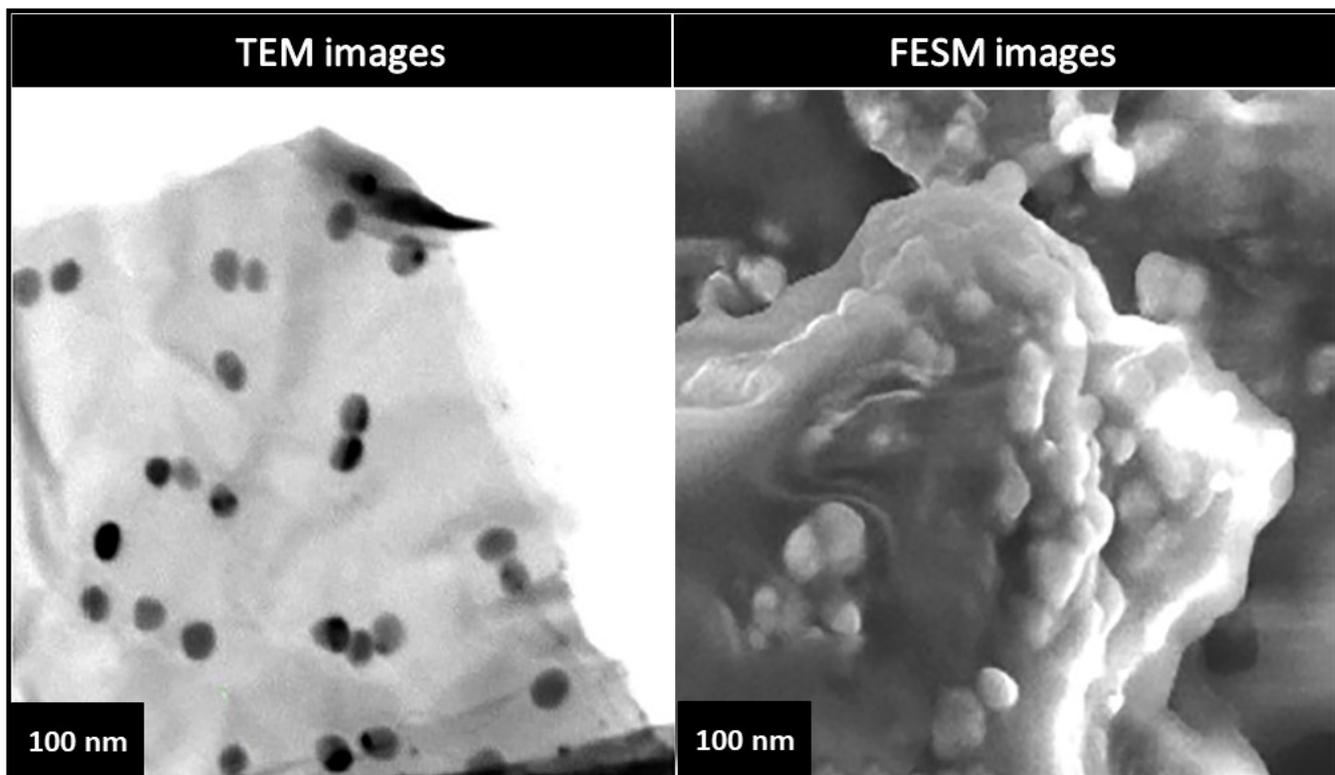


Figure 15. The TEM and FESM images of nanoparticles Graphene oxide-silicon dioxide (GO-SiO₂). Reprinted with permission from ref. [47]. © 2016 Elsevier B.V.

4. UF Membranes Applications in Oily Wastewater Treatment

Among all applications of UF membrane, it has been widely applied for wastewater treatment especially for oily wastewater applications. Table 7 shows the summary of the UF membrane applications in oily wastewater. For example, the PVDF-based UF membrane was fabricated by Yuliwati et al., using $\text{LiCl}\cdot\text{H}_2\text{O}$ and TiO_2 as embedded materials in PVDF solution for the application of refinery wastewater treatment. TiO_2 with (1.95%) and (0.98%) of $\text{LiCl}\cdot\text{H}_2\text{O}$ in PVDF solution results in achieved water flux of (82.5 $\text{L}/\text{m}^2 \text{ h}$) and (98.8%) oil rejection. The permeate flux reduced significantly when the TiO_2 is excess over (0.98%), due to poor dispersion of TiO_2 in the membrane matrix [58]. A similar study using the PVDF membrane was conducted by Liu et al. In their study, the polyaniline PANI-modified PVDF membrane was utilized for oily wastewater treatment, and they found the water flux up to 3000 $\text{L}/\text{m}^2 \text{ h}$, high oil rejection, and high and steady flux of water permeation [59].

Moreover, the role of sulfonated polyphenyl sulfone (SPPSU) with the existence of the MgO nanoparticle for the oil/water emulsions treatment was investigated by Arumugham et al. [60]. The membrane made by using (25 wt.%) SPPSU/MgO leads to an enhanced flux recovery ratio (FRR) to (94.9%) due to the improvement of the hydrophilicity of the SPPSU/MgO membrane, which gives high oil rejection ($\geq 99\%$) and a water flux of (234 $\text{L}/\text{m}^2 \text{ h}$) [60].

In other studies carried out by Gohari et al. [61] and Kumar et al. [62], they used the PSf membrane for the treatment of an oil/water emulsion. Gohari et al. used hydrous manganese oxide (HAO) nanoparticles blended with the PSf membrane and enhanced the rejection (R) to ($\sim 100\%$) and a water flux of (1194 $\text{L}/\text{m}^2 \text{ h}$) by using a HAO:PSf weight ratio of (2:1) [61]. However, Kumar et al. found that the impact of 10–15 wt.% in the CS on the PSf results in enhanced R with a reduced permeate flux due to the reduction in the porosity of the membrane [62].

Ahmad et al. fabricated the PVC/DMAc/bentonite membrane to enhance the performance of the PVC-based UF membrane for the treatment of oily wastewater with an oil concentration 200 ppm. At 6.0 wt.% bentonite in the CS, an enhanced PVC membrane performance with water flux (186 $\text{L}/\text{m}^2 \text{ h}$) was obtained due to the pore density, porosity, and hydrophilicity of the membrane [63].

In addition, PES MMM blended with hydrous manganese oxide (HMO) nanoparticles prepared by Gohari et al. for oily wastewater treatment (containing 1000 ppm oil) found a high water flux of (573.2 $\text{L}/\text{m}^2 \text{ h}$), an oil rejection of ($\sim 100\%$), and a FRR of (75.4%) [17].

The impact of varying concentrations of polyethylene glycol (PEG) on the morphology and performance of the PAN UF membrane was studied by Panda et al. [64]. At a PEG concentration of (0.08 g/g), the water flux was enhanced to (60 $\text{L}/\text{m}^2 \text{ h}$), and the water flux reduced to (50 $\text{L}/\text{m}^2 \text{ h}$) with a further increase in PEG concentration [64].

Table 7. Shows the summary on the UF membrane applications in oily wastewater with membrane characterization and performance.

| Polymer | Additives | Preparation Technique | Oil Concentration (ppm) | Membrane Characterization | | | Performance | | | Reference |
|-----------|--|-----------------------------|-------------------------|---------------------------|---------------|---------------------|---------------------------|-------------------|-------------------------------|-----------|
| | | | | Qi % | Contact Angle | Mean Pore Size (nm) | Flux (L/m ² h) | Oil Rejection (%) | Flux Recovery Ratio (FRR) (%) | |
| PVDF | TBC | RAFT | 1000.00 | - | 71.00° | - | 60.50 | 99.00 | 67.00–78.00 | [2] |
| PVC | TiO ₂ -NPs | - | 40.41 | 79.50 | 62.50° | 77.00 | 116.00 | 96.30 | 89.90 | [4] |
| PVDF | LiCl·H ₂ O/SiO ₂ | MMM | - | 85.41 | 50.00° | 34.05 | 82.50 | 98.83 | 81.70 | [38] |
| PVDF | LiCl·H ₂ O/TiO ₂ | - | 17.00 | 85.41 | 47.33° | - | 82.50 | 98.80 | 98.83 | [58] |
| PANI/PVDF | PANI | dilute polymerization | - | - | - | 25.00 | 3000.00 | - | - | [59] |
| PPSU | SPPSU/MgO | NIPS | 1000.00 | 65.70 | 48.90° | 24.00 | 234.00 | 99.00 | 94.90 | [60] |
| PSf | PVP/HAO | NIPS | 100.00–1000.00 | 87.20 | 8.00° | 48.98 | 1194.00 | ≈100.00 | 67.00 | [61] |
| PSf | PVP | NIPS | 100.00–400.00 | 37.00 | 60.00° | - | 90.00 | >90.00 | - | [62] |
| PVC | Bentonite | NIPS | 200.00 | 78.64 | 55.10° | 118.90 | 412.00 | 97.00 | 81.97 | [63] |
| PES | PVP/HMO | NIPS | 100.00–1000.00 | 87.90 | 16.40° | 76.40 | 573.20 | 100.00 | 75.40 | [17] |
| PAN | PEG | NIPS | 100.00–1000.00 | - | - | - | 60.00 | 90.00 | - | [64] |
| PES | PDA@ZnFe ₂ O ₄ NCs | NIPS | 500.00 | - | 52.00° | 69.00 | ~687.00 | - | ~82.50 | [65] |
| PVC | PAN/PF127/bentonite blended | Single-step phase inversion | 200.00 | - | 0.00° | 89.00 | 790.12 ± 40.15 | 97.25 ± 1.35 | 82.90 | [26] |

5. Conclusions

Considerable efforts are being undertaken in finding effective technologies for oily wastewater treatment. Membrane technology is one of the promising methods for treating oily wastewater. Among all types of membrane technology, ultrafiltration (UF) is considered to be a versatile separation process and purification process. It is commonly used to treat oily wastewater with <400 ppm oil content and <20 μm oil droplet size.

However, its widespread use requires improving the characteristics of polymer membranes in order to solve the problems of clogging. For the separation of oily wastewater, the low-cost super hydrophilic polymeric UF membrane with enhanced morphology and mechanical strength is in high demand. As a result, low-cost PES, PVC, PSf, and other polymers may be employed as a basis polymer.

Several methods of polymer alterations were used to improve hydrophilicity, antifouling membrane ability, and oil rejection, including polymer blending, membrane surface modification, and the mixed membrane matrix. Since fouling usually occurs on the surface of membrane, surface modification is one of the most reliable and simple methods to apply. The main purpose of membrane modification is to provide high permeate flux and hydrophilicity, improve surface morphology, and thus improve membrane performance.

Moreover, another approach has been tried to improve the performance of polymeric membranes with a beneficial effect by using additives such as inorganic nanoparticles, hydrophilic polymers, and amphiphilic and grafted copolymers. Popular inorganic particles that have been repeatedly used to fabricate membranes are SiO_2 , TiO_2 , Al_2O_3 , MgO , GO , etc. Their use in membranes has significantly improved their antifouling properties with respect to oil products.

This means that it is possible to prevent pollution of the environment with highly toxic oil products and to provide a source of clean water for recycling the water supply.

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Abbreviations

| | |
|----------|--|
| AFM | atomic force microscopy |
| APTES | 3-aminopropyltriethoxysilane |
| ATRP | Atom transfer radical polymerization |
| CNTs | Carbon nanotubes |
| DI | Deionized water |
| EDMA | Ethylene glycol dimethacrylate |
| EIPS | Evaporation induced phase inversion |
| FRR | Flux recovery ratio |
| F-MWCNTs | Functionalized-multiwall carbon nanotube |
| GMA | Glycidyl methacrylate |
| GO | Graphene oxide |
| HNTs | Halloysite nanotubes |

| | |
|------------------|---|
| HMO | Hydrous manganese oxide |
| HAO | Hydrous manganese oxide |
| MgO | Magnesium oxide |
| MMM | Mixed matrix membrane |
| MPD | M-phenylenediamine |
| MWCNT | Multiwall carbon nanotubes |
| NPs | Nanoparticles |
| NMP | N-methyl-2-pyrrolidone |
| NIPS | Non-solvent induced phase inversion |
| PIP | Piperazine |
| PDDA | Poly (diallyl-dimethylammonium chloride) |
| PDH | Poly (dimethylaminoethyl methacrylate-co-2-hydroxyethyl methacrylate) |
| PMMA | Poly (methyl methacrylate) |
| PNIPAAm | Poly (N-isopropylacrylamide) |
| PPEGMA | Poly (oligo ethylene glycol methacrylate) |
| PSS | Poly (sodium 4-styrenesulfonate) |
| PVA | Poly (vinylalcohol) |
| PAN | Polyacrylonitrile |
| PA | Polyamide |
| PAI-SPEEK | Polyamide imide-sulfonated poly (ether keton) |
| PANI | Polyaniline |
| PES | Polyethersulfone |
| PEI-CuNPs/PAA | Polyethyleneimine-CuNPs/poly(acrylic) acid |
| PPSU | Polyphenylsulfone |
| PSf | Polysulfone |
| PVC | Polyvinyl chloride |
| PVDF | Polyvinylidene fluoride |
| PVP | Polyvinylpyrrolidone |
| R | Rejection coefficient |
| SEM | Scanning electron microscopy |
| SiO ₂ | Silicon dioxide |
| SSLbL | Spray-and spin-assisted layer-by-layer |
| SPPSU | Sulfonated polyphenyl sulfone |
| SPC | Sulfonated polycarbonate |
| TIPS | Thermally induced phase inversion |
| TFC | Thin film composite |
| TiO ₂ | Titanium dioxide |
| TMC | Trimesoyl chloride |
| UF | Ultrafiltration |
| VIPS | Vapor induced phase inversion |
| ZnO | Zinc oxide |

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