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Review on Membranes for the Filtration of Aqueous Based Solution: Oil in Water Emulsion

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Abstract

This review provides insight into the application of membrane technology in the filtration of aqueous solution generated from different industries. Due to the ever-evolving and demanding strict attention to rules and regulation for discharging of oily waste water, researchers have investigated membrane technology as a best and suitable method for separation of oil in oil-water emulsion. Membrane-based separation processes are becoming a novel material to treat oily wastewater due its facile operation process and effective in removal of oil from oil/water emulsion. This review summarizes or highlights the recent development of advanced membrane technology employed to separate oil in water emulsion using polymer and ceramic-based membranes and modified membranes via blending, coating, grafting and other techniques. Moreover, integrated membranes system to achieve high separation efficiency over single membrane process is also discussed. Perspective and conclusions concerning the future development of filtration membranes for treatment of oil in water mixture are also provided. A review of membrane technology for oil/water emulsion treatment could have a substantial contribution in developing novel membranes and modification of the existed membranes.

Keywords Novel material; Oil/water emulsion; Membrane technology; Oily waste water

Abbreviations: MF: Microfiltration; NF: Nano Filtration; UF: Ultrafiltration; RO: Reverse Osmosis; WCA: Water Contact Angle; OCA: Oil Contact Angle; IMS: Integrated Membrane System; CA: Cellulose Acetate; PVP: Poly Vinyl Pyrrolidone; NMP: N-Methyl-2-Pyrrolidone; PES: Polyethersulfone; PEI: Poly Ethyleneimine; PAN: Polyacrylonitrile; PSf: Polysulfone; NIPS: Non-solvent Induced Phase Separation; PTFE: Polytetrafluoroethylene; ENF: Electrospun Nanofibrous

Introduction

Background

With increasing industrial development and rapid population growth, discharging of oily wastewater from the activity and process of different industries such as, petrochemical, beverages, metal-finishing, metallurgical, food industries etc. is increasing at alarming rate, causing unprecedented harm to natural environment and human being and this is due to the fact that oil is flammable and also can decompose to form other harmful chemical, further aggravating pollution in the environment and adversely affects aqueous habitants and human's health [1-6]. Besides, Oily waste water is one of the factor that cause water pollution, which can have a concentration of 100-5000 mg/L or higher, depending on the nature of crude oil [7]. Based on the environmental guidelines, however, the maximum discharge limit of the total oil and grease allowed is 10-15 mg/L. Development of efficient, environmentally friendly and cost effective methods for treatment of oily waste water is highly demanded, yet still challenging [8-10]. As a result, it is a serious issue in the world and oily waste water treatment is a global challenging task which is urgently needed.

Environmental protection policy has led to many industries to invest efficient technologies to treat oil/water mixture and minimize organic pollutants before discharging it into the environment. Though, there are different conventional oily wastewater treatment methods such as, gravity separation, skimming, heating, ultrasonic separation, electrocoagulation, centrifuges, settling tanks and ignition of oil, these techniques are useful for filtration of oil/water unstable emulsion and mixture, they are subjected to many limitations such as, low efficiency, high cost operation, producing secondary pollutants, unable to remove efficiently microns or submicron sized oil droplet, corrosion and recontamination problems [11-13].

This requires a novel material that can efficiently and effectively filter oil/water from the mixture of oil-water (o/w). The development of low-energy separation technologies for oil/water emulsion is therefore indispensable and has received an attention in the last few decades [14]. Application of membrane technology for oily wastewater treatment is becoming a promising method because of its high efficiency, relatively low operation cost and chemical durability, steady quality of permeate and space requirement compared to traditional separation processes [15-16]. Transmembrane pressure is a driving force for this technology, which allows the passage of emulsified mixture by a porous system, causing retention of oil on the surface of the material [17].

Legion kinds of membrane processes including Microfiltration (MF), Nano Filtration (NF), Ultrafiltration (UF) and Reverse Osmosis (RO) have been recently employed for oil/water separation. In practical scenario, it is important to preferential maintain one phase at the surface of the membrane and keep the membrane from fouling, and to consolidate this, two types of surface wettability are employed. These are surface membrane with super-hydrophobic and super-oleophilic or surfaces with the inverse wettability that are super-oleophobic and super-hydrophilic. When such surface membranes are fabricated and subjected to oil/water mixture, it preferentially attract one of the phase in order to reduce the overall interfacial energy of the system [2].

However, membrane fouling, which is extremely complex phenomenon, is becoming a major problem that hampers the application of membrane technologies. This can be caused by numerous factors such as, deposition of oil droplets and other undesirable molecules at the surface of the membranes or inside the pores, resulting deterioration of the membrane, decrease the life time and finally limited productivity or even blockage of the membrane from filtration of the desired products [18].

Many researchers have reported that increasing membrane surface hydrophilicity could effectively enhance the permeability, inhibits oil droplets from adsorption to the surface and substantially decrease membrane fouling tendency, and numerous studies have demonstrated several approaches to increase the hydrophilicity and fouling resistance of the membranes such as, blending, coating, grafting and others [19-23], resulting a high polarity and less hydrophobic. A hydrophilic membrane surface is one which has a low Water Contact Angle (WCA) and hinders deposition of undesired substance (foulants) due to steric repulsion [20].

In this review paper, recent advances in the membrane technology, techniques used to modify the existed membranes to exhibit super-hydrophilicity are provided. Additionally, the Integrated Membrane System (IMS) as optimal separation efficiency is also discussed.

Fundamental Knowledge of Oil-Water Mixture

Oil properties

Oil properties play a key role during separation and removal of oil from oil/water mixture emulsion. Oily wastewater generated from various industries is a complex in composition and compounds in wastewater can include free, dispersed, emulsified and dissolved oil and dissolved minerals. The main contaminants in wastewaters produced from petroleum industry sectors such as, refineries are oils and greases and are classified in to four forms based on their droplet size (d, diameter): emulsion, dispersion and free mixture with droplet size of $d<20$ μm, $20<d<150$ μm and $d>150$ μm respectively and the forth is dissolved oil (not in the form of droplets). Oil is a mixture of hydrocarbons such as, toluene, benzene, ethylbenzene, xylene, polyaromatic hydrocarbons and phenol, while dissolved formation minerals are inorganic compounds (anion and cation including heavy metals) [3,21,22].

Moreover, readers are recommended to infer the following articles for a comprehensive fundamental properties of oil/water mixture such as, classification oil/water mixture based on different criteria [23-28], desirable properties of emulsion [29-31], usual lab based emulsion employed for testing of membranes [32-35], concept of surfactant [25,27-29] and different types of oil/water emulsion [30-33].

Membrane Technologies for Oil Water Separation

Membrane based separation was started in petroleum industry for treating of produced water since 20th century [33]. Membrane based separation of oil/water mixture received much attention and many researchers have involved in designing and fabricating of novel membrane with different route of preparation. Membrane technology shows attractive performance in treatment of oily waste water compared to traditional techniques as the separation is very easy such that the membrane act as semi-permeable layer between the two phases of oil and water and the membrane selectively filter from the two phases. These membranes can be made of polymer, inorganic compounds or composite and the leading membrane types in laboratory application are polymer based membranes [34].

The most common polymer materials used to prepare MF, NF, RO or UF are Polyethersulfone (PES), Polyacrylonitrile (PAN), Poly (P-Phenylene Sulfide) (PPS), Polyvinylidene Fluoride (PVDF),) Polysulfone (PSf), polycarbonate and Cellulose Acetate (CA). Due to their high efficiency to separate mixtures like emulsified and dispersed oils, [35] low energy requirement during operation and inexpensive compared with ceramic based membranes, polymer membranes have been used extensively in many applications [8,36,37].

Membrane types and materials

Membrane filtrations are becoming increasingly universal for purification of waste water from ground and surface and also in desalination and treatment of oily waste water. Oily waste treatment processes mainly employs four types of pressure driven membranes: MF, NF, UF and RO, membranes. Membranes are capable of removing a wide variety of undesired molecules, ranging from large colloids, Algae and bacteria that have magnitudes of micrometers and ions that have hydrated radius of Angstroms [38]. In this review, the most common membrane types, MF and UF, used in separation of oil in water emulsion are presented and the main differences among the different types of membrane-filtration processes is also provided.

Understanding of the sources of oil in oily wastewater, the characteristics of the oil presented in the waste, the concentration of the oil and suspended solids in the raw wastewater, the presence of oil-wetted solids, temperature and pH that impacts the type and size of selected oil water separator, temperature and material selection for oil water separation equipment and the need of the treatment are factors that helps to select the appropriate separation system [22].

Microfiltration (MF): Microfiltration membrane is one type of membrane filtration that is widely used in oil-water separation. It is generally defined as the pressure-driven flow of a suspension containing colloidal or fine particles with dimensions within the size range of 0.1-10 μm through a membrane, using these membranes to separate an emulsion of oil in water is a well-established process. Commercial MF membranes made from various thermoplastic polymers such as, PSf, PES, Poly(Vinylidene Difluoride) (PVDF) and PAN are used extensively for aqueous feed streams [39]. Many MF membrane works were reported, that demonstrates their effectiveness in treatment of oil in water emulsion. Carpintero et al. [40], employed polyester/nylon, silicon nitride micro sieves and Polycarbonate Track Etched (PCTE), Anodisc, CA membranes of different pore sizes (0.22-0.8 μm) for treating of oil-water emulsion. To enhance the hydrophilicity of the PCTE membranes and micro sieves, respectively Poly Vinyl Pyrrolidone (PVP) and hydrogen peroxide were used and the others mentioned membranes were hydrophilic. The membrane microstructure and surface properties were pointed out as the main factors that affect separation performance. After extensive experiment, it was found that the micro sieve membrane exhibits high water flux due to high hydrophilicity resulting from the structure modification. In general, the membranes performance in separation of oil/water

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emulsion was reported as follows: micro sieves>CA>Nylone>PCTE>Anodisc.

Another studies, Suresh et al. [41] employed cross flow MF to treat oily wastewater using ceramic support and TiO_2 membrane. Using uniaxial compaction method, clay based ceramic membrane support with mixture of pyrophyllite, quartz, feldspar, kaolin, ball clay, calcium carbonate and PVA as a binder was prepared. TiO_2 composite membrane was prepared using hydrothermal method using TiO_2 sol derived from $TiCl_4$ and NH_4OH solution. Compared to ceramic support, TiO_2 composite membrane exhibited high capability of treating oil in water emulsion attributed to hydrophilic surface of the TiO_2 membrane. TiO_2 membrane showed oil rejection as high as 99%. Some studies improved the efficiency of the membrane by controlling the operating parameters rather than modification of the membrane itself.

Pan et al. [42] employed TiO_2 dynamic membranes in separation of oil-in-water emulsions via cross flow MF. When the temperature was increased, steady permeate flux was promoted. The optimal preparation condition was determined to be 0.5 g/l of the emulsion concentration, 1.13 m/s of the feed flow rate and 0.125 MPa of the preparation pressure. The study results show that oil rejection efficiencies are as high as 98% with the permeate concentrations less than 8.3 mg/L.

Ultrafiltration (UF): Ultrafiltration membrane is a pressure driven membrane process which can concentrate and fractionate macromolecular solutes and separate suspended species from water [23]. Several types of UF membranes for oily waste water treatment have been studied. Kumar et al. [43] developed an UF membrane by blending of PSf as base polymer, PVP as additive and N-Methyl-2-Pyrrolidone (NMP) as solvent using phase inversion technique. The study reported that the prepared membrane was effective in separating of oil/water mixture when the composition of PSf, PVP and NMP was 15%, 5% and 80% respectively. Researchers used Zetasizer to estimate the average size and the size distribution of oil droplets. The concentration of oil in water can be also measured using a UV-vis spectrophotometer [44].

Researchers have modified the hydrophilicity of the PES hollow fibre UF membrane by using carboxyl, hydroxyl and amine modified Graphene Attached Poly Acrylonitrile-Co-Maleimide (G-PANCMI) and evaluated its performance for separating of oil/water emulsion. The results show that the G-PANCMI plays a key role in promoting the hydrophilicity, selectivity and permeability of the PES membrane. The WCA and Oil Contact Angle (OCA) of the PES membrane was changed from 63.7 to 22.6 and 43.6 to 112.5, respectively and it was reported that the development of PES-G-PANCMI membrane as a promising method to separate oil in water emulsion [45]. There are also other appropriate UF membranes which are mentioned in the following.

In another study Melbiah et al. [46] reported an UF membrane of flat sheet PAN was used for the separation of oil-water emulsion mixture, which was fabricated by Non-solvent Induced Phase Separation (NIPS) process with combination of amphiphilic copolymer Pluronic F127 (PF127) and inorganic calcium carbonate ($CaCO_3$) nanoparticles. Upon the addition of 0.75 wt% of $CaCO_3$ nanoparticles to the membrane, the membrane properties were optimized, with flux recovery of 63%-93%. The study suggested modification of the existed membrane could contribute for high efficiency separation. PAN was further modified by other researchers and is presented as follows.

A study reported a novel PAN UF membrane was used in treatment of oil/water emulsion which was fabricated by hydroxylamine-induced phase inversion process, possessing high hydrophilicity (Figure 1). The membrane displays a high flux ranging from 2200 to 3806 L/m^{2}h bar and remarkable separation efficiency obtained for oil in water emulsion. Besides, the PAN membrane shows good recyclability and high fouling resistance due to ultra-low oil adhesion property and the study reported, PAN UF membrane as a promising potential for treatment of oily wastewater [47].

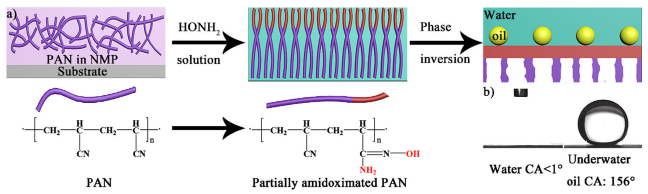

Figure 1: a) Formation of a super-hydrophilic/underwater super-oleophobic PAN membrane by a hydroxylamine-induced phase-inversion process. **b)** Photographs of a water droplet on the membrane showing a contact angle of <10° (left) and an underwater oil droplet on the membrane showing a contact angle of 1560° (right), adopted from [47].

Membranes are considered as a prominent technology to treat oily wastewater due to its simplicity, ease of operation and low energy. Extensive efforts have been employed towards membrane preparation for the application of oil/water mixture separation. MF and UF are the current candidate membrane utilized in the filtration of oil/water emulsion. To compare those two mentioned types of membrane for the future potential application, we should consider numerous scenarios such as, the current efficiency, cost, fouling phenomena, backwashing and others.

A comprehensive list of various MF membranes utilized for oil-in-water emulsion separation is reported in many literatures [48-57]. Moreover, UF membranes utilized in this application are also actively researched and readers are recommend to infer for detail analysis of the respective membrane information such as, employed method to prepare the membrane, efficiency, fouling compromise, potential of oil/water separation and others [44,45,58-65,66].

It is not straightforward circumstance to mention membrane which could be potentially candidate and utilized in the future for separation of oil/water emulsion. We should consider the various factors (cost-low pressure driven membrane MF but UF-efficient for small emulsion of oil in water, but high pressure driven membrane than MF, fouling phenomena which is dependent on the material used to prepare the respective membrane). In general, compromise settlement should be considered during identification of the best membrane for the intended application.

Recent Advances in Membrane Technology

Nowadays, many researchers involved in modification of the existed membrane to increase its performance for oil/water emulsion separation. Membranes are prone to fouling that deteriorates their performance. Many studies have investigated surface modifications as best option to lessen these phenomena. This review paper provides a comprehensive overview on potential (Surface) modification techniques for various membranes such as, blending, coating and electrospinning, composite and other modification techniques.

(Surface) modification of membranes

In oil/water emulsion separation, the surface chemistry of the membrane is required to be hydrophilic that binds water better than other molecules and also high hydrophilic helps to prevent the membrane from fouling. Oil and other particles in the mixture have hydrophobic interaction with water and the oil content in the mixture should be less than 50% such that the water is continuous phase and the oil in dispersed phase. Oil and other particles in the feed stream tend to coalescence and leads fouling in the membrane process. To minimize fouling, the membrane requires a surface chemistry that prefers binding to water better than other materials. UF and MF membranes are the most commonly used in separation of oil/water mixture and many researchers attempted to make the surface of the membrane to withhold of high hydrophilicity properties, but the membranes are still experiencing fouling problem.

Recently, there are different mechanisms used to enhance the performance of membrane's flux and antifouling properties. Many researchers have attempted to improve the antifouling and hydrophilicity of the polymeric membranes by surface modification and other techniques are some of the methods are descried as follows [23,67,68].

Blending: Blending of two or more materials could result in a new type of material with remarkable characteristics. The blend membranes have an excellent performance and mechanical properties compared with the original or pristine membrane and many studies reported the blended membrane as a novel material due to their optimized surface structure and performance. Due to its facile preparation, favored to incorporate desirable characteristics on the membrane and remarkable properties to modify the membrane, polymer blending has been used to fabricate novel membrane using a phase inversion process [69]. Hydrophilic additives such as, PEG and PVP can be utilized to enhance the porosity and hydrophilicity of the membrane.

Polymer poly-(dimethylaminoethyl methacrylate-co-2-hydroxyethyl methacrylate) (PDH) was synthesized as a zwitter ionic polymer precursor and used as an additive in the preparation of zwitter ionic PVDF membrane. Zwitter ionic additive was embedded in the membrane using the in site cross-linking to make the membrane stable and proceeds with sulfonation to transform the precursor to zwitter ionic polymer. A zwitter ionic PVDF/PSH-blend membrane with super-hydrophilic and underwater superoleophobic properties has been successfully fabricated by NIPS process. When the fabricated membrane was subjected to oil/water separation, it exhibits a high permeability of water and after the experiment the recovery of water flux was more than 98% showing that remarkable antifouling performance. Steps in the formation of the membrane are shown in Figure 2 given below [70].

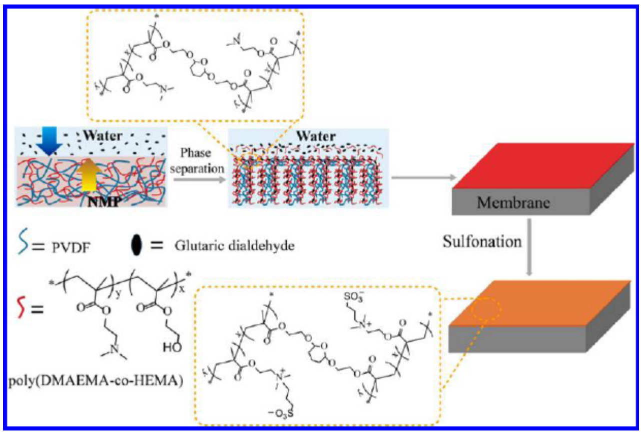

Figure 2: Schematic description of phase separation in the formation of zwitte rionic PVDF/PSH-blend membranes using random PDH copolymer as an additive, combined with *in situ* cross-linking and subsequent sulfonation, adopted from Zhu et al. [70].

Another finding provided an effective route for separation of oil/water emulsion by blend electrospinning of PLA with P34HB. PLA membranes are highly hydrophobic and water cannot permeate through it and in contrast P34HB has hydrophilicity property, thus, the membranes consisting of blend fibers exhibited superior water permeability from oil/water emulsion under gravity. To investigate the effect of addition of P34HB in the fiber diameter, relative viscosity of the solution and conductivity were measured and the result showed that with incorporation of P34HB in the solutions, the conductivity increased but the relative viscosity was reduced. Electrospun membranes are efficient in the separation of oil/water emulsion under gravity due to relative pore size and high porosity [71].

In another studies, Zhou et al. [72] employed activated carbon for the treatment of emulsified oily wastewater. Using different packing materials and blend system of the modified activated carbon and resin, the efficiency of the separation oil/water emulsion was investigated. Cetyltrimethyl-ammonium bromide-modified polystyrene resin (R-CTAB) was fabricated and its performance of oil removal was compared with Granular-Activated Carbon (GAC) and polypropylene granular (pp). The result shows that the modified polystyrene resin has a remarkable oil removal performance in different operation conditions and this was due to the hydrogen bond interaction between hydrocarbon and the hydrophilic part of the surfactant. The report also suggest, hybrid system of R-CTAB+GAC can remove most of the oil from the emulsified of oil/water, which resulted in more than 90% reduction of oil content in permeate.

Moreover, by incorporation of amphiphilic copolymers in the polymer matrix was an adopted method to prepare desirable properties of blend membrane. This helps the amphiphilic copolymer to be synthesized flexibly [68]. Separation of oil in water using another novel membranes called PES membranes modified with copolymer pluronic F127 was adopted. Due to the additives of pluronic F127, the surface of PES has enhanced its hydrophilicity, subsequently high permeate flux and good antifouling property-exhibited. Pluronic F127 as surface modifier largely decreased the WCAs of the PES/Pluronic

F127 membranes showing that the blended membrane has higher hydrophilicity [19].

In general, blend membrane have showed better route to separate oil/water emulsion. The hydrophilic nature of the inorganic metal oxide and the better mechanical strength of the polymer combined, results in efficient oily waste water treatment. On the other hand, blend membranes were lagging in commercialization due to their own defects. Dispersion of nanoparticles symmetrically, inability to control pore size and leaching phenomenon of the nanoparticles are the main limitation blended membranes. Further research and development is highly required to eliminate the aforementioned drawbacks.

Coating and electrospinning: A process where a coating material creates a thin layer to the substrate with non-covalently bonded is known as coating [20]. Coating process and electrospinning are relatively low cost and simple, and therefore suitable for many application [73,74]. The membrane fouling which is the main limitation in membrane separation technology can be minimized to some extent by surface modification methods. This can be done by binding of some additives to the surface either by chemical techniques such as, acid base treatment, coating and grafting or physical techniques such as, plasma irradiation, ion beam irradiation and vapor phase deposition [68]. Modification of membrane surface mainly gives an effort to minimize the fouling by reducing the interaction of unwanted chemicals to the membrane surface and increase the permeability of the desired product. Chengui et al. [75] studied surface modification of PVDF membrane via amine treatment and resulted up to 57% of the fluorine on the membrane surface elimination by the amine treatment, which contributed to increase hydrophilicity of the membrane surface accompanied with antifouling enhancement.

Researchers An et al. [76] reported Janus Membranes with Charged Carbon Nanotube Coatings for De-emulsification and filtration of oil-in-water Emulsions. This membrane presented as a kind of competent material for the separation of o/w emulsions due to its nice adjustment of the surface nature for the hydrophilic and hydrophobic layers. Janus membranes were simply prepared from negatively or positively charged CNT coating and hydrophobic polypropylene MF membranes by vacuum filtration.

A study reported a surface fabricated by coating silica nanospheres onto a glass fiber membrane through sol gel process, showed super-hydrophilic and underwater superoleophobic surface. The membrane has a complex framework with micro and nano structures exhibiting a high efficiency (>98%) of oil-in-water emulsion separation under harsh environments high salt concentration and acidic medium. The membrane did not show a decline efficiency, which provides outstanding stability and was recommend as a best candidate in the application of oil/water emulsion separation [77].

Li et al. [78] prepared two PMMA-b-PNIPAAm (Poly(methyl methacrylate)-b-Poly(N-isopropylacrylamide)) based smart membranes with temperature modulable oil/water wettability through solution-casting method and electrospinning technology, respectively. PNIPAAm modified surfaces can reversibly switch between hydrophilicity and hydrophobicity when the temperature fluctuates below and above its Lower Critical Solution Temperature (LCST). When the temperature is below the LCST of PNIPAAm at 15°C, the membrane exhibit high hydrophilicityand in contrary when the temperature was above LCTS of PNIPAAM at 50°C it shows high hydrophobicity which generally proved the prepared membrane was a switchable.

Electrospun fibrous membrane exhibits higher fluxes of about 9400 L/m^2h for water and 4200 L/m^2h for oil. Solution-casting membrane shows water flux of about 6200 L/ m^2h and an oil flux of about 1550 L/m^2h. Nano-particle of TiO_2 with inherent hydrophilicity were successfully incorporated on to the surface of PVDF polymer membrane to improve its hydrophilicity property. Uniquely mussel-inspired method was modified by introducing a silane coupling agent KH550, the ability to bind nanoparticles was retained and the membrane changes from normal state of hydrophilic to super hydrophilic state and as result ultra-high efficiency (99%) and good oil resistance and antifouling capability was obtained. This novel membrane shows high water permeation flux and display profound recyclability [79]. In some studies, prepared module membrane modification was reported and particular example is provided as follows.

A recent study reported that surface modification of Polytetrafluoroethylene (PTFE) hollow fiber membranes based on co-deposition of Polymerized Dopamine (PDA) and Poly (Ethyleneimine) (PEI) from aqueous solutions could effectively filter oil/water mixture. After PDA and PEI were successfully deposited on PTFE membranes, the hydrophilicity and wettability of the modified membrane were highly enhanced. The study provides a one-step method to enhance the hydrophilicity and chemical stability of the PTFE hollow fiber membranes for application of oily waste water treatment [80].

An Electrospun Nanofibrous (ENF) membrane with hierarchical structures which was prepared by the construction of polydopamine nanoclusters onto a cross-linked PAN/hyperbranched polyethyleneimine (PAN/HPEI/PDA) ENF membrane was reported to separate oil/water emulsion under gravity. The PDA nanoclusters coated on membrane surface enabled the ENF membrane to exhibit super hydrophilicity with a low WCA of 0°, and underwater superoleophobicity with a high OCA of 162°, reaching high flux(~1600 L/m^2h) and high oil rejection (98.5%) and showed excellent antifouling properties in oil/water separation [73,81]. In more intense, a prominent membrane with switchable properties was reported.

Furthermore, a novel membrane with switchable superwettability for oil and water was reported. This novel membrane was developed by electrospinning of porous Polyvinylidene Fluoride (PVDF)-silica composite nano/micro-beaded top layer and a PVDF nanofibrous intermediate layer on a non-woven support. The membrane is a switchable in which under-oil Superhydrophobic, in-air superamphiphilic, and underwater superoleophobic. It showed a high flux up to 2000 L/m^2h and high separation efficiency (>99.99% in terms of water and oil purities in the permeation) with remarkable robustness under harsh circumstance. Besides, an excellent antifouling and easy washing properties was obtained [8]. Moreover, a self-cleaning Piezoelectric Membrane for Oil-in-Water separation was reported by Mao et al. [82].

Another oil-water separation method via coating enhanced membrane was reported by Gondal et al. [13]. They investigated the effect of spray coating of nanostructured WO_3 on stainless steel meshes and compared with ZnO coated mesh in separating of oil-water emulsion. It was reported that WO_3 coated stainless steel mesh exhibited high separation efficiency (99%) than ZnO coated surface. Due to the fact that nanostructured WO_3 is a well-known catalyst, the photocatalytic degradation of organic pollutants found at permeate from the oil/water mixture were tested using WO_3 coated surfaces under UV radiation and the performance of the degradation was profound.

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Note that, membrane modification via coating have owned a lot of advantages to enhance morphology and other properties of the membrane though, the stability of the coating on the membrane during execution of the oil/water separation is main concern.

Grafting: One of the chemical surface modifications of membrane, grafting (grafting to and grafting from) was utilized to enhance the performance of the membranes. 'Grafting to' is performed by grafting of end functionalized polymer chain to the solid surface whereas 'grafting from' is performed by polymerization of monomers from the surface. The former grafting method is easy to control and characterize by synthesis whereas the second grafting method is difficult to control and characterize [68]. Many experiments reported that surface grafting as an effective surface modification of many membranes due to its easy and versatile approach to enhance the surface properties of the membranes. The capabilities to alter the polymer surface to have useful properties, controlled addition of graft chain with specific localization and high density on the surface and long term chemical stability are the main advantages of grafting.

A smart PVDF-g-PAA tree-like nanofiber membrane with pH-responsivity was fabricated via simple homogeneous solution polymerization and electrospinning Poly(Vinylidene Fluoride)-graft-Poly(Acrylic Acid) (PVDF-g-PAA). In acidic water the membrane became hydrophobic/superoleo-philic, whereas in neutral water, the membrane showed superhydrophilicity/underwater oleophobicity. The as-prepared membrane functioned on-application of oil/water separation using gravity alone by switching the pH of the medium. Tetrabutylammonium Chloride (TBAC), N, N- Dimethylformamide (DMF), acetone, Polyethylene Polyamine (PEPA), Acrylic Acid (AA), Potassium Peroxodisulfate (KPS), 1, 2-dichloroethane (DCE) were used to prepared this smart membrane (Figure 3) [83].

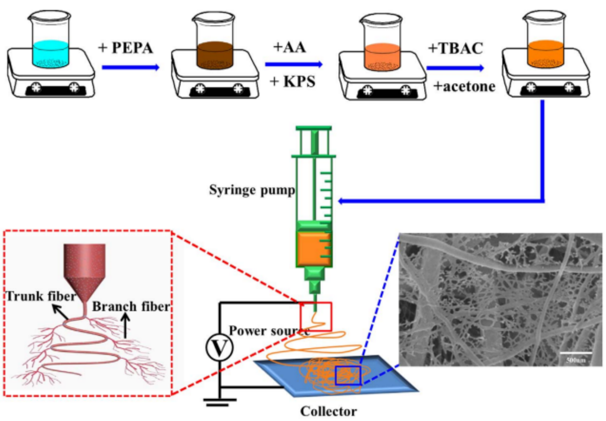

Figure 3: Schematic illustration of procedure for preparing pH-responsive PVDF-g-PAA, tree-like nanofiber membranes [83,92].

Yuzhang et al. [84] employed a pH-induced non-fouling membrane prepared by grafting hyper-branched PEI onto PVDF/polyacrylic acid grafted PVDF blend membrane surface via simple amidation reaction for effectively separating of oil in water emulsion. The superhydrophilic and underwater superolephobic PEI grafted membrane exhibits high flux with excellent fouling resistance so that it maintains stable flux and this novel membranes was suggested as a promising method for treatment of acidic oily waste water.

Study reported that oily waste water can be treated by PVP grafted polyvinylidene fluoride (PVDF) UF membranes. The PVDF membranes were chemically modified by grafting PVP via a three-step reaction: defluorination process, double bond hydration process and PVP graft process in which the PVP is put into the polyalcohol membrane surface by hydrogen bond interaction. The results show that the PVDF-PVP membranes separation performance of oil in water was enhanced compared with pristine PVDF and the fouling phenomenon was studied and found that external fouling is the root cause of flux decline and cleaning with NaOH greatly improved the performance of the membrane [5]. Many membranes were modified via grafting and more examples are provided as follows.

Grafting-of-poly(N-isopropylacrylamide)-(PNIPAAm)-block-poly(oligoethylene-glycolmetha-crylate) (PPEGMA) nanolayers to modify low molecular weight cutoff regenerated cellulose UF membranes using surface-initiated Atom Transfer Radical Polymerization (ATRP), intended to prepare fouling resistance surface was reported. The modified membranes rejected the undesired molecules up to 97% though permeability was reported to be reduced by 40%. But after comparing of the final flux, it was reported that over 40 h cross flow filtration run, the altered membranes exhibited a 13.8% higher cumulative volume water than the pristine membrane [85].

A membrane material which consists of copolymer of hydrophilic CA and hydrophobic PAN segments was synthesized through grafting PAN onto CA powder via free radical polymerization for the application of oil water separation. Method of grafting of PAN on to CA was done by free radial polymerization using cerium ion redox system and applied to fabricate the UF membranes by phase inversion method [86]. Using this blended membranes high oil/water emulsion flux and complete oil rejection, as well as the remarkable flux recovery property have been obtained. In another work, a novel thiol covered polyamide (nylon 66) MF membrane was prepared by combining mussel-inspired chemistry and coupling reaction, which has dual-function i.e., efficient oil removal and mercury ion adsorption from waste water was obtained. The co-deposition of PDA and PEPA on membrane made the membrane to exhibits high hydrophilic and enhanced the permeability [87].

A charged poly (vinylidene fluoride) (PVDF) membranes were used for oily wastewater treatment which was obtained by grafting modification techniques using addition-induced polymerization. Ethylene glycol dimethacrylate (EDMA) and Glycidyl methacrylate (GMA) were used as initial monomers and after graft polymerization the former was sulfonized with sodium sulfite. The modified membrane were allowed to separate oil/water emulsion and it was reported that 98% of oil rejection obtained with low fouling (<16.6%) and insignificant irreversible fouling during UF test [88].

Note that, the membrane modified via various grafting techniques (chemical imitated, plasma initiated, enzyme initiated etc.) show high fluxes and in some cases attractive oil repellent character. Furthermore, modification method is very mild and environmentally friendly compared to the more traditional methods, provided that it works at room temperature and it uses O_2 and H_2O and no releasing of toxic chemical to the environment.

Composite: A composite is a material made from two or more materials which differ in chemical or physical properties and remain independent and unique on macroscopic level within the finished structure [23]. Many researchers have involved in separation of oil/water emulsion using a composite membrane. A study reported the application of α-alumina-/polyamide 66 composite membrane in the rejection of oil from oil-water emulsions. The α-alumina ceramic tubes were impregnated internally with a solution of polyamide 66 (PA66) (5% w/v) and tested with oil solution and distilled water. However, the water flux was decreased because of the presence of PA66 layer on the inner surface of the support. The membrane was prepared by dip-coating from polyamide 66 solution (PA66) inside the tubular ceramic support (pore diameter of 0.65 μm). Ceramic support rejected the oil in a range of 43.3 to 92.3% and the membranes of one and two layers of polyamide 66 showed oil rejection of 53.8 to 97.7%, and 78.5% to 99.5%, respectively [17].

Yahui et al. [26] fabricated a composite membrane of PAN nanofibers with nanocrystalline Zeolite Imidazole Framework (ZIF-8). When the composite membrane was tested using emulsifier stabilized oil-in-water and water-in-oil emulsions, the membrane displayed high flux and separation efficiency, and good recyclability. The composite membrane was fabricate by ectrospinning and is shown in Figure 4 below. The membrane exhibits pre-wetting-induced super-oleophobicity under water and super-hydrophobicity under oil. The hybrid membrane shows a high OCA under water (159°) and high WCA under oil (155°), representing multifunctional materials for oil/water emulsion separation. In this study, UV-Vis spectrometry was used to analyze the purified water.

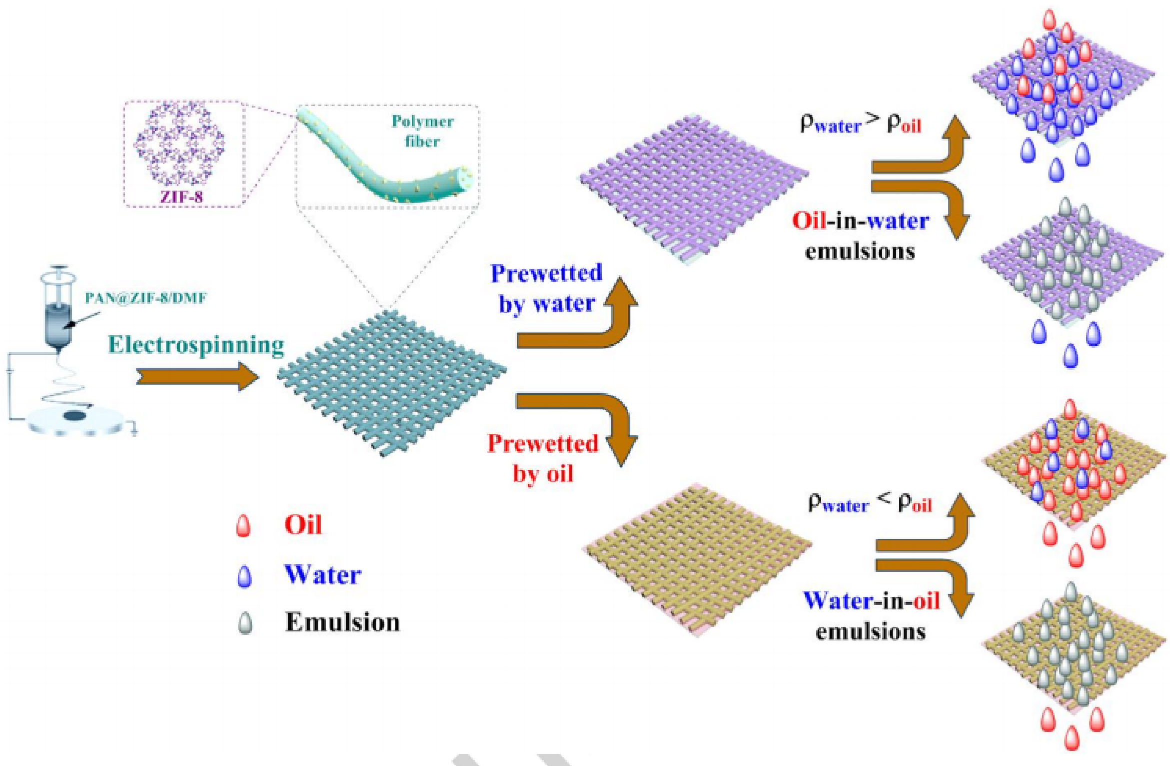

Figure 4: Fabrication of the PAN with ZIF-8 composite membrane and selective separation of oil/water mixture and emulsion adopted from [26].

Composite membrane of PTS/PSf was prepared using additive of Phosphorylated TiO_2-SiO_2 (PTS) particles with good hydrophilicity which were synthesized by the sol-gel method and added to PSf through phase inversion method. The PTS particles were uniformly dispersed in the PTS/PSf composite membrane and the membrane increased its hydrophilicity and antifouling than the PSf, SiO_2/PSf and phosphorylated Zr-doped hybrid silica (SZP)/PSf. The result showed that, PTS/PSf composite membranes, under 0.1 MPa I water flux was 116 L/m^{2}h with oil retention of 92%, WCA was reduced from 78.0° to 45.5° and the membrane was effective in separation of oil/water mixture [16]. However, this membrane shows high WCA and other studies reported with less WCA than this membrane.

Another study demonstrated that PAN/Graphene Oxide (PAN/GO) composite fibers was fabricated by facile electrospinning and then was hydrolyzed (H-PAN/GO) for tailoring their chemical features, and the fabricated membranes was subjected to oil-water emulsion to evaluate its performance. The result showed that H-PAN/GO membrane with GO concentration at 7% (H-PAN/ GO7%) is superhydrophilic in air and ultralow-oil-adhesion under water. As a result, the H-PAN/GO7% membrane's flux was high (~3500 LMH), with rejection (~99%) and remarkable flux recovery ratio (~99%) for separating oil-water emulsion [89].

Ngang et al. [7] employed thermo-responsive polyvinylidene fluoride/silica-poly (N-isopropylacrylamide) (PVDF/SiO_2-PNIPAM) composite membrane for treatment of oil/water mixture. It was reported that the composite membrane showed lower oil adsorption tendency in pure water compared to the neat PVDF membrane due to the hydrophilic nature of PNIPAM.

Composite MF membrane (poly vinyl acetate (PVAc)-coated N6/SiO_2) prepared by electrospinning technique exhibits high hydrophilicity with high mechanical strength and decreased roughness surface due to the nanoparticles of SiO_2, interconnected complex structure of N6 nanofiber mats and PVAc coating respectively. The MF membrane was fabricated using the techniques called electrospinning.Due to the increment of hydrophilicity, the permeability of PVAc-coated electrospun N6/SiO_2 composite membrane was higher than the pristine N6 membrane. The report showed that a water flux of 4814 LMH/bar and as high as 99% oil rejection at oil concentrations of 250 mg/L, 500 mg/L and 1000 mg/L was achieved. Besides, fouling resistance of the PVAc-coated N6/SiO_2 composite membrane was much higher than that of the commercial PVDF and PSf due to hydrophilicity increment and PVAc antifouling property. Moreover, stability of the fabricated membrane was enhanced due to the interaction electrospun nanofiber mat and the PVAc [12].

Hou et al. [90] developed composite membranes using electrospinning with a hydrophobic substrate and a hydrophilic top surface to alleviate the oil fouling phenomenon in membrane distillation. PTFE hydrophobic substrate was coated with two different hydrophilic fibrous networks (CA plus polymer-nanoparticle composite silica nanoparticles (SiNPs)). Of the two types of surface coating prepared, it was reported that the CA-SiNPs coating was more attractive than the CA coating in developing the oil fouling resistance as the SiNPs experience hydrophilicity in-air and oleophobicity under water. Using this membrane, it was effective in separation of oily waste water with profound performance.

Note that, similar to the method of blending, composite membrane utilized for oil/water separation are lagging from commercialization due to many factors such as, losing of flux during operation and susceptible for fouling.

Other treatment techniques: In addition to the aforementioned techniques of modification of membranes to enhance their hydrophilicity, there are various techniques that could help to modify existed membranes to the desired properties and are provided as follows.

Carbon Nanotube (CNT) nano-hybrid membrane modified by polymer mediated surface charging and hydrophilization via vacuum assisted self-assembly process was fabricated to improve antifouling property and water permeability. The result showed that the new fabricated membranes exhibited a high water permeation reaching up to 4592 L/m^2h bar, exceeding by 10 folds of commercial UF membrane used for separation of oil/water emulsion. Different types of polymers PEI, Chitosan (CS), Polyacrylamide (PAM), Polyvinyl Alcohol (PVA) and others were used to fabricate the polymer-CNT Nano-hybrid membrane. The results manifested that the deposition of oil droplet to the membrane surface is weak as a result less fouling phenomenon was occurred. In general, the antifouling properties of as-prepared membranes, PVA based CNT had high antifouling properties than the others due to of high hydrophilicity and weak electrostatic interaction with oil droplets. The water permeability rate of the membranes showed relatively stable and at the range of 3100-4600 L/m^2h bar, and the flux of the membranes reduced when the thickness of polymer on CNT increased and this is due to filling of the network of the CNT by the more polymer that leads to minimize the pore size, according to the literature of [18].

A another report showed that incorporation of additives of PVP and Polyethylene Glycol (PEG) in PVDF-TiO_2 membrane greatly enhanced the hydrophilicity of the membrane and more than 99% oil rejection was obtained. Two different polymeric solutions were formulated: PVDF-TiO_2/PVP/DMAc (M1), PVDF-TiO_2/PEG/DMAc (M2) and comparing the two formulated polymers, M1 and M2, M2 membrane with additive of PEG exhibited better performance than M1 due to the good inherent material composition and preparation [91].

Researchers have reported that PSf membrane modification with PVP and PEG leads to increase its performance for separation of oil/water emulsion. With combination of PSf/NMP/PVP, PSf/DMAc/PVP, PSf/DMAc/PEG) and PSf/NMP/PEG different types of membranes were fabricated stating that the polymer (PSf) concentration was set at 12% and the remaining percent covered by the additives and the solvent. Results show that PSf membranes prepared with PVP/NMP and PEG /DMAc have good permeate flux compared to the membranes prepared with PEG/NMP and PVP/DMAc combinations. This can be due to the difference of morphological structure with different molecular weight of the additives [65].

PVDF electrospun modified membrane was fabricated using a Triethylamine (TEA) as a modifier. Due to its low surface tension (20.66 m N/m) it improves the hydrophilicity of the membrane and also TEA leads to release fluorine in the form of HF and hence the modified membrane can attract water molecules easily. The results showed that the membrane has an excellent performance for separation of the tested oils in water mixtures.

It was reported that after hydrothermal treatment of PVDF using TEA and water, the new membrane exhibited 23,564 and 29,923 LMH water flux of hexane in water and gasoline in water, respectively which is much higher than the conventional membrane [67]. PVDF membrane surface modified by polydopamine was also reported for separating oil/water emulsion [11].

Researchers employed a nano-hybrid PES membranes containing SiO_2 and ZnO for produced water treatment in a double stages configuration. The nano-hybrid PES membranes were prepared via dry-wet NIPS technique to form flat sheet membranes. In this study, the first stage used nano SiO_2 and nano ZnO incorporated to PES matrix to produce nano-hybrid and the second stage used neat PES without any additive (Figure 6) [92]. It was reported that the nano-hybrid PES-nano SiO_2 membrane exhibits 25% higher permeate flux than the nano-hybrid PES-nano ZnO. The application of double stages configuration of nanoparticles hybrid PES membrane improved the permeate flux by 200% and pollutant rejection efficiency by 16-18%.

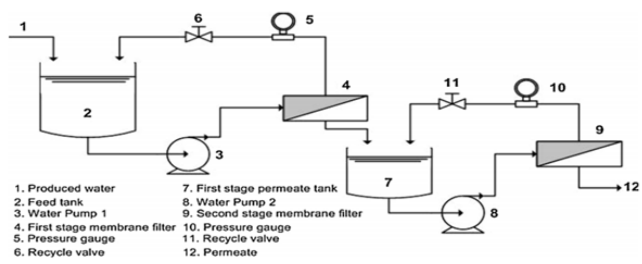

Figure 6: Cross flow double stages membrane filtration.

Membrane biofouling can be minimized by modification of the membrane surface with Ag nanoparticles. Silver-loaded PAN hollow fibers were prepared via the dry jet-wet spinning technique from a dope containing 0.5 wt. % silver nitrate. The result showed that at Agloading of 0.1 wt. % bacteria growth for both *E. coli* and *Staphylococcus aureus* (*S. aureus*) was not observed on the membrane surface. The antibacterial activity of the modified membrane is attributed to trace amounts of silver ion released from the fiber [93].

A modified PSf membrane was also used in oil/water separation which was prepared by phase inversion method. By incorporation of polymeric additives such as, PEG, PVP, polyetherimide (PEI) and PES, they exhibited high permeability, good antifouling property and high rejection coefficient during oil-water mixture separation [94].

Many literature such as, a flexible nonvolatile resistive switching memory device based on ZnO film fabricated on a foldable PET substrate [81], hollow fiber membrane for cross flow MF of oily waste water [95], and other articles [45,96-142] are among the comprehensive finding that discloses the available membrane technology employed in separation of oil/water emulsion.

To conclude about the various surface modification methods of membranes mentioned before, blending modification techniques showed a high and permanent hydrophilic modification than physical modification-coating. However, it is not always easy to compare and figure out the appropriate modification method since parameters are highly dependent on the environment where they are operated and could be influenced by one modification method otherwise; I provide the general comparison and summary of the modification methods.

Development of inorganic membrane

Though polymeric membranes are the leading membrane type in oil/water separation application (Table 1), ceramic membranes are also used to overcome the problem associated with polymeric member such as, low mechanical strength, instability in chemical and thermal treatment, and sensitive to bio-fouling and others. As a result, ceramic membranes are remarked as the best an alternative material to replace polymeric membranes in harsh condition applications due to their stability under chemical and thermal treatment [34]. Recently, inorganic membranes have been developed for the application of oily waste water treatment [23].

Name of membrane	Fabrication/modification techniques	Additives/component used	Performance/efficiency	Reference
Zwitterionic PVDF/PSH	Blending/in situ cross-linking/NIPS	PDH	98% flux recovery high flux of water	[19]
PLA/P34HB	Blend electrospinning	PLA	Superior water flux	[20]
PES	Dry-wet NIPS	SiO2/ZnO	High flux, 200% Pollutant rejection, 16-18%	[70]
PVDF	Electrospinning	Silica composite	Flux, 2000 L/m2	[8]
PSf	Blending	PVP and PEG	good permeate flux	[69]
PVDF-TiO_2 membrane	Blending	PVP and PEG	99% oil rejection	[68]
PES/Pluronic F127 membranes	Blending	pluronic F127	higher hydrophilicity good antifouling property	[17]
PSf	Phase inversion	PEG,PVP,PEI and PES	high permeability, high rejection coefficient	[72]
PTFE	Deposition/coating	PDA and PEI	Enhanced hydrophilicity and chemical stability	[59]
PMMA-b-PNIPAAm	Solution-casting method and electrospinning	PNIPAAm	fluxes 9400 L/m^2h	[58]
PVDF	Coating	NP of TiO_2	Ultra-high efficiency (99%)	[30]
ENF	Cross-linking/Coating	PAN/HPEI/PDA	high OCA of 162° flux=1600 L/m^2h	[55]
Stainless steel meshes	Spray coating	NP of WO3	High separation efficiency (99%)	[11]
PVDF	Grafting	PVP	Easy to clean via NaOH Excellent fouling resistance	[5]
Cellulose UF	Grafting of PNIPAAm- PPEGMA, ATRP	PNIPAAm- PPEGMA	97% oil rejection 13.8% higher flux than pristine	[61]
PVDF-g-PAA	Polymerization and electrospinning	PAA	pH-responsivity showed super-hydrophilicity	[60]
PVDF	Amidation reaction	PEI	high flux with excellent fouling resistance	[29]
PAN-g-CA	Grafting/free radical polymerization	PAN	Enhanced its hydrophilicity	[63]
PVDF	Electrospinning	TEA	Flux >23,000 LMH	[51]

PAN/GO	Facile electrospinning	GO	flux around 3500 LMH rejection of 99%	[66]
PVDF/SiO_2-PNIPAM	Radical polymerization	PNIPAM	lower oil adsorption tendency	[7]
PAN	Electrospinning	ZIF-8	high flux and separation efficiency, OCA=1590	[65]

Table 1: Summary of recent polymeric membrane used in oil/water emulsion separation.

Ceramic based membranes have been used to separate colloidal, oil, sub-microns and micro size suspended particles from wide range of fluids. Over the past few years, many researchers have given an attention on the development of high performance ceramic membranes with low cost. Ceramic membranes have an advantages of well-defined pore size distribution compared with polymer and can achieve high permeability, thermal stable material and possible to wash with harsh chemical without affecting the membranes performance [68] and long life, good de-fouling properties. Though, ceramics membranes have numerous advantages, there is still no report on large industrial application and this can be due to low oil rejection efficiency, liable to membrane fouling and high demand of cost [23].

Research on ceramic membranes was initially focused the preparation of alumina membranes. Currently, numerous porous membrane materials such as, zirconia, alumina, titania and silica have been developed to fabricate ceramic membrane. Among these, zirconia is very attractive for inorganic membranes. The profound quality of zirconia based membrane includes high chemical resistance and good water permeability, high thermal stability [23].

Commercially available Al_2O_3 MF membranes was modified to reduce the membrane fouling due to oil droplets, using nano sized ZrO_2 as coating to obtain an attractive properties of inorganic properties. It was reported that coating of Al_2O_3 improved the hydrophilicity of the ceramic membrane. By using oil/water emulsion as feed, the steady flux of the modified ceramic membrane was obtained in a short period of time. The steady flux keeps 88% of the initial flux and the oil rejection is higher than 97.8%. The decrease in membrane fouling by oil droplets attributed to the enhancement of membrane hydrophilicity by the by nano-sized coating, the proper cross flow velocity and back flushing [68].

Liu et al. [143] employed a hydrophilic-controlled MFI-type zeolite-coated mesh for oil/water separation. It was prepared on porous stainless steel mesh by *in situ* and secondary growth method. The zeolite mesh contains a polyhedral crystals showing of high hydrophilicity, which absorbed water passing through the mesh driven and rejected oil simultaneously. To enhance the hydrophilicity of the zeolite-coated mesh, Al3+ ions were introduced into the zeolite structure resulting high oil/water separation performance. The oil rejection rate of the membrane becomes as high as 99% with the water flux of greater than 80,000 L/m^2h at the ratio of 0.04, Al/Si.

The MFI-type zeolite-coated mesh were used to separate many kinds of oil such as, n-hexane, cyclohexane, mineral oil and vegetable oil and mesh exhibit's more than 96% rejections for all these oils. The *in situ* grown method shows time and energy saving to fabricate the MFI-type zeolite without loss of membrane performance compared with the secondary grown membrane.

Based on the studies report, among the commonly used metal oxide ceramic membrane zirconia membranes showed slightly higher flux than alumina and titania membrane. Moreover, membranes with pore sizes of 0.1 μm could provide an outstanding oil/water separation in terms of optimized flux and permeate quality. As summary, Performance evaluation of different kinds of inorganic membranes for desalination and oily wastewater treatment is provided in [144].

Integrated Membrane System (IMS)

An IMS can be defined as a system that integrates two or more membrane processes or as a system combining a membrane process with other treatment processes [145]. IMS combines different individual units with their respective properties to achieve a high separation efficiency over single membrane process. Many IMS such as, integrated MF and RO (MF-RO), UF and RO (UF-RO), UF and membrane distillation (UF-MD and forward osmosis and membrane distillation (FO-MD) systems were reported for oily water treatment [145].

In integrated MF-RO, UF-RO and UF-MD systems, MF and UF were firstly used as pretreatment process to remove oil from oily water to a great extent. After MF and UF treatment, some amount of oil was still detected in permeate. Then, the aforementioned IMS functioned as enhancement treatment process for further removal of oil in the permeate [146].

To date there are various IMSs treatment for oily waste water treatment. Waynet et al. [147] reported an advantage of an IMS of MF/UF as pretreatment process before use of RO. This reduce the rate of colloidal fouling of a RO system though it may not necessarily reduce the rate of organic fouling but could be effective if the RO membrane is made of polyamide (low fouling composite).

Dongwei et al. [148] utilized integrated UF-FO-MD system for dual purpose, for treatment of oil/water mixture and desalination application. This system efficiently treated both oily water and sewage, and obtained high pure water. Oil contents of oily water greatly influenced the membrane performance and fouling of FO-MD subsystem, while its temperature and salt content had slight influence. The study reported that oily waste water treated using integrated UF-FO-MD system meets the injection water standard and for oil production purpose the oil can be re-circulated.

Moreover, Somayeh et al. [149] employed hybrid UF/RO membrane separation process for treating of oily waste water released from oil refinery. The UF membrane was made of PSf, a hydrophilic flat sheet membrane and Ro membrane was a spiral wound thin film made of composite polyamide. UF was used primarily to remove the emulsified oil droplets in the mixture followed by RO to remove total dissolved solids. The role of operating parameters such as, cross flow and TMP were investigated in UF in pretreatment. The report result showed that UF membranes removed more than three forth of oil and was considered as an effective treatment. Remove as high as 95% from the effluent, this kind of IMS was suggested as the promising method to treat oily waste water.

Membrane Characterization and Fouling Test

To examine the morphology of the membrane, Field Emission-Scanning Electron Microscopy (FE-SEM) with a platinum coating on the sample surface and Transmission Electron Microscopy (TEM) can be employed. Using ImageJ software, it is possible to investigate the pore size and the pore distributions of the membranes by processing of the Image of FE-SEM [12]. Hydrophilic property of membrane can be evaluated by WCA (goniometer) with automated dispensing system [16], In-air water, in-air oil, underwater oil [44] and under-oil WCAs [150] techniques can be used. The surface chemical composition of membrane can be analyzed by Fourier Transform Infrared Spectroscopy (FTIR) [47], Atomic Force Microscope (AFM) measure the surface morphology (roughness), the Young's modulus and the interaction force between the oil droplets and the surface of modified membranes [18]. X-ray Photoelectron Spectroscopy (XPS) and Attenuated Total Reactance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) are helpful to analyze the elemental composition and covalent bond structures of the coated membranes.

To test the fouling property of the prepared membrane, dead-end and cross flow tests are used to investigate the flux recovery and decline for the modified and pristine membrane. Besides, a study reported that anionic and non-anionic surfactants should be used to stabilize emulsions treated by cross flow and dead-end batch filtration, respectively [21]. A metallographic microscope was reported to observe the size and content of oil droplets in oil-in-water emulsion [11]. To investigate the concentration of oil in water, a UV-vis spectrophotometer can be employed [44].

Another route to estimate the separation efficiency of the fabricated membrane is using Thermal Gravimetric Analysis (TGA) which is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. Since the mixture of oil and water differs in their boiling temperature, it is possible to estimate the purity of permeate by heating to 105°C provided that only water will be evaporated and the oil portion will not be [151].

Furthermore, there are variety of techniques that are commonly used to measure contact angles, including the Wilhelmy balance method, conventional telescope-goniometer method, and the more recently developed drop-shape analysis methods [152].

Estimation of membranes performance: To estimate the performance of the membrane, it is possible to use mathematical expression for different parameters such as, water flux, rejection ratio, and Flux Recovery Ratio (FRR), Flux Decay Ratio (FDR). The water flux Jw1 (L/m^2h) is calculated by the following equation [19].

$$Jw=V/A\Delta t$$

Where, V=flow rate; A=membrane area; t=permeation time

To evaluate the antifouling property of any novel membranes, the oil/water emulsion FDR can be calculated using the following expression and the lower DR value shows membrane's fouling resistance property [19].

$$DR=((Jw-Jp)/Jw_1)) \times 100\%$$

Where, Jw_1=water flux-1, Jp=steady flux

In order to evaluate the antifouling properties and the efficiency of membrane refreshing by different cleaning fluid, Flux Recovery Ratio (FRR) can be calculated using the following expression and the higher FRR value represents membrane's better antifouling ability and higher washing efficiency [19].

$$FRR=(Jw_2/Jw_1) \times 100\%$$

The oil rejection ratio can be calculated using the following expression [19].

$$\text{Rejection Ratio}=(1-C_p/C_f) \times 100\% \quad (4)$$

Where, C_p and C_f are the oil concentrations in permeate and feed solutions, respectively

Membrane cleaning: After the membranes executed certain separations, it needs to be cleaned as it could be subjected to fouling phenomenon, thus cleaning will regenerate membranes to its initial performance depending on the chemical agent used to clean it. Researchers have been used numerous cleaning agent to maintain the membranes performance .Backwash with hot water and hot alkali solution, alkaline wash followed by acidic wash, or the micellar solution of sodium dodecyl sulfate-n-pentanol-water system are among the commonly used [153]. A short cleaning cycle to get rid of some cake formation on the layer of the membrane includes backwashing, air flushing and ultrasound. For NF membrane, a report suggested hydrochloric acid as a best cleaning agent at concentration of 0.20% w/w [154].

Conclusion and my Perspective

In conclusion, membrane separation processes have become an emerging technology for separation of oil/water mixture emulsion due to its facile operation process, operate without heating, and high efficiency in removal of oil component from the mixture. In this review, more focus was given to the recent development of membranes including polymer, ceramics and novel material fabricated by modification of the existed membranes by various methods such as, blending, coating, and grafting. A summary with general comparison of the different surface modification is provided, which I presented it based on the literature results. Furthermore, integrated membranes system for oil/water mixture separation was considered as appropriate option to overcome problem faced by other methods. Membrane fouling, selectivity and low flux have attracted the attention of numerous researchers, scientists and practitioners.

Despite continuous improvements and developments, the main challenges that still need to be addressed to facilitate the market demand of membrane technology are fouling control and flux aspects. Researchers have attempted to minimize the fouling phenomenon by developing of innovative antifouling membranes using different routes such as, increasing of the hydrophilicity of the membrane by coating, blending, composting and grafting, provided that the modified membrane hinders the oil from depositing to the surface of the membrane. Another route was developing of inorganic membrane that could offer high water flux and less fouling phenomenon. A variety of different inorganic membranes with attractive surface wettability for separation of oil/water emulsion applications have been fabricated. Many researchers have also attempted to enhance membrane performance by controlling the operating parameters such as, flow rate, transmembrane pressure, temperature, concentration and others. However, mitigating of the fouling problem is still worldwide challenging. Moreover, ongoing research to overcome these challenges has recommended solution such as, adequate pre-treatment step, development of novel material, development of new cleaning agent that optimize the cleaning procedure and the utilization of Nano-sized particles to fabricate smart membranes.

There are many researches going on oily wastewater treatment. Some UF and MF processes exhibited a profound potential in the removal of oily wastewater treatment and use of UF and MF to treat oil-water emulsions is anticipated going to rise in the future. Implementation of membrane technology in oil wastewater treatment is limited due to its low flux as a result of fouling properties. In general, many researchers agreed that enhancing of the hydrophilicity of the membranes could prevent the deposition of the oil in the surface of the membrane and subsequently the fouling phenomenais reduced and water permeability of the membranes would be favored. Some of my perspective points toward membrane technology in filtration of aqueous solution (oil in water emulsion) for the future trends are presented as follows.

- In oily waste water, there is diverse quantity of compounds and a single membrane could not be used to remove and treat the mixture. Conventional separation techniques coupled with membrane technology can be an effective and novel approach for treatment of oil/water mixture emulsion.
- Though many researchers have been involved in modification of the current membranes, further surface modification for the current existed membranes and designing and fabricating of a new novel material that are environmentally friendly is highly demanded.
- In addition to polymeric membranes, researchers shall focus also on ceramic membranes with affordable cost to prepare hydrophilic membrane as those shows chemical, thermal resistance and other fascinating properties.
- The integrated membrane approach has recognized as a promising technique and is also a plausible way for the future too, in separation of oil/water mixture emulsion effectively with minimization of its capital cost. The influence of the feed stream on the IMS should be further researched in detail considering its complex composition. Moreover, investigation on the membrane fouling modification and development of inherently fouling resistance is highly needed to enhance the membrane antifouling ability and performance of the IMS.
- It is anticipated that research on the treating of oil/water mixture using membrane material will continue. Nevertheless, more research is demanded to develop super-hydrophilic membrane accompanied with high selectivity, high flux and high resistance to fouling.

Although many challenges are in the future, Integration of different membranes owns a great potential for the separation of oil/water emulsion with super-hydrophilic surface. I anticipate a continuous development of membranes via surface modification that exhibits controllable super-wettability in the coming decades, which will be comparatively indispensable approach to effectively treat oil/water mixture.

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