

Review on Liquid–Liquid Separation by Membrane Filtration

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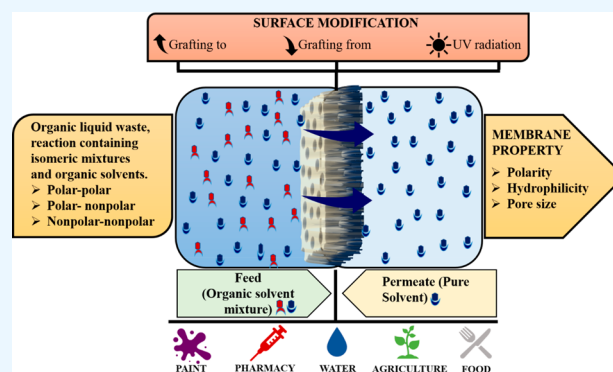
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ABSTRACT: Liquid–liquid separation is crucial in the present circumstances. Substitution of the conventional types of separation like distillation and pervaporation is mandatory due to the high energy requirement of the two. The separation of organic mixtures has a huge potential in industries such as pharmaceutical, fine chemicals, fuels, textile, papers, and fertilizers. Membrane-affiliated separations are one of the prime techniques for liquid–liquid separations. Organic solvent nanofiltration, solvent-resistant nanofiltration, and ultrafiltration are a few methods through which organic liquid–liquid separation can be attained. Implementation of such a technology in chemical industries reduces the time consumption and is cost efficient. Even though a lot of research has been done, attention is needed in the field of organic–liquid separation aided by membranes. In this review, various membranes used for organic mixture separations such as polar–nonpolar, polar–polar, and nonpolar–nonpolar are discussed with a focus on membrane materials, additives, separation theory, separation type, experimental setup, fouling mitigation, surface modification, and major challenges. The review also offers insights and probable solutions for existing problems and also discusses the scope of research to be undertaken in the future.



1. INTRODUCTION

Solvents account for 80–90% of the total organic mixture used in any organic reaction and contribute to 80–85% of the waste.¹ Organic compounds are found to have a plethora of applications ranging from mining industries to pharmaceutical industries. Therefore, the purification and separation of these solvent molecules has become very important to encourage purification or to enhance reusability. It was found that 80% of the pharmaceutical wastes are organic solvents; hence, treatment of waste involving organic moieties is a pervasive challenge faced by the industries. The recent techniques used for the removal of organic pollutants are waste liquid coal slurry (coal slurry), biohydrogen production by anaerobic bioconversion of organic liquid waste by recirculation of digester effluent (bioH), cation-exchange resin regeneration waste liquid by enhancing anaerobic fermentation of organic matters (resin), etc. The cost required to achieve the same is about 40–80% of the capital and operational cost combined. Therefore, there is a need to inculcate more efficient separation techniques to meet the energy- and cost-related demands.² The separation of organic solvents is one of the foremost challenges in membrane separations. The commonly used solvents in organic synthesis are aliphatic hydrocarbon, aromatic hydrocarbon, cyclic hydrocarbon, amines, ketones, esters, ether aldehydes, etc. It is inevitable for organic synthesis to occur without the presence of organic solvents. The choice

of organic solvent required for a particular synthesis depends on various properties of solvents such as hydrophilicity, viscosity, polarity, density, boiling point, etc.³

Membrane technology is found to be very handy in such situations, due to its low energy consumption when compared to distillation and evaporation which leads to thermal damage of heat-susceptible organic molecules (Figure 1).^{4,5} Although there have been a lot of innovations and ground-breaking research in the field of membrane technology, there still lies considerable room for innovative thinking in a broader perspective.⁶ On the other hand, organic solvents have a rising demand in the global market which paves the way for reuse and recovery of waste. The challenge faced in this field is that most of the membrane material remains labile in contact with few organic solvents, thereby narrowing the use of the usual polymers. Techniques such as cross-linking or post-treatment are done to enhance the stability of membranes in solvents but with a trade-off of permeate flux.⁷ Various other factors such as membrane pore size, hydrophilicity, viscosity of

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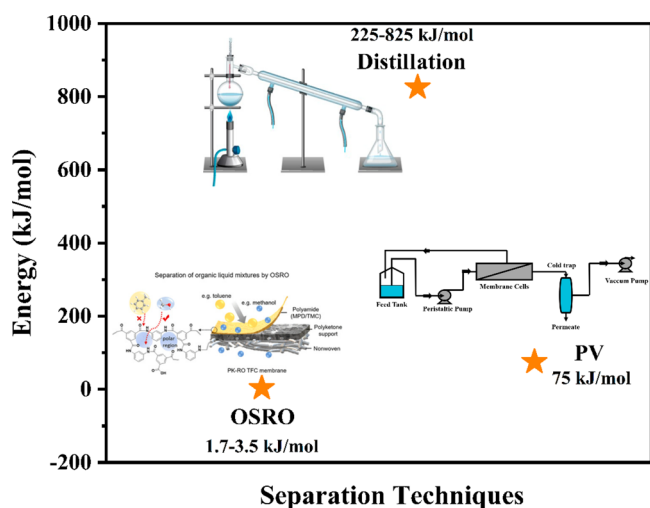


Figure 1. Energy requirement in various separation processes.

the membrane dope solution,⁸ molecular size of the solvent, hydraulic permeance of the organic solvent,⁹ etc., influence the membrane performance to a greater extent. Organic solvent reverse osmosis (OSRO), organic solvent nanofiltration (OSN), and solvent-resistant nanofiltration (SRNF) are a few streams as far as organic separation is concerned which demand further investigation. With the advent of a more solvent-inert membrane and new material, with high probability one can definitely say membrane technology can replace all the conventional separation techniques.

Membrane separation is well established, showcasing separations ranging from oil–water separation,¹⁰ metal rejection,¹¹ biotechnology, pulp and paper, pharmaceutical, food processing, petroleum, and desalination.⁶ The functioning of a membrane depends on various factors which act as driving forces, such as pressure, temperature, electrical, or concentration difference, etc.¹² Use of membrane technology for liquid separation is found to be more efficient because of its high potential to minimize the energy usage involved in purification and separation. This boon embraced by membranes extends its scope of application to gas- as well as liquid-phase separations. Conversely, membranes are prone to swelling and have poor chemical stability due to their weak or reversible chemical bonds, and a general strategy such as cross-linking is used to improve the structural stability of traditional polymers.¹³ Also, we know that in membrane technology there lies a trade-off between selectivity and permeability during separation.¹⁴ These two factors determine how fast and to what extent the molecule of interest travels across the membrane. Achievement of high flux enables permeability of a large volume of fluid through the membrane at a given time, whereas as high membrane selectivity favors delivery of the desired products with high purity. The benchmarks set are (i) to surpass the upper bound of permeability–selectivity trade-off and (ii) design membranes prone to less fouling, physical aging, and chemical aging.¹⁵ In addition, liquid–liquid separations (of organic molecules) have a trade-off between high affinity (sorption or selectivity) and deterioration of the selective layer due to swelling. Compared to conventional methods, membrane filtration has gained the potential to overcome all the above-mentioned hurdles and has also been found to be environmentally compatible and involve less energy and operational time.¹⁶ Solvent-stable polymers

such as polyimides, polysiloxanes, polyphosphazenes, etc., are a few specialized polymers⁶ used for separation. Most reverse osmosis (RO) and nanofiltration (NF) membranes used in the treatment of water, coming from various sources, have different salinity, natural organic content, and biological matter. The transport of molecules across membranes is best explained by size exclusion and the solution-diffusion mechanism.¹⁵ Most of the separation techniques such as distillation, extraction, evaporation, and forward and reverse osmosis rely on high thermal energy, have poor stability, and are expensive devices.

Membrane researchers have persistently developed new NF polymeric and ceramic membranes. Each of these membranes has their own pros and cons. Polymeric membranes are easily modifiable and accessible but are slightly unstable in a few organic solvents. Ceramic membranes are found to be more expensive than polymeric membranes, and due to the hydrophilic surface of polymeric membranes, they tend to repel out organic solvent though they are chemically inert and rigid in organic medium as desired. Ceramic membranes have resilience toward high temperature and harsh organic solvent over polymeric membranes. The main obstacles observed in OSN membranes are (i) specific and consistent molecular weight cutoff and (ii) predicting the membrane performance based on interactions between the membrane, solvent, and solute. All these complications have paved the way to more innovations in order to tackle the separation and purification of organic solvents. When inorganic additives are amalgamated with polymeric materials, we have what is known as mixed matrix membranes (MMMs). Ceramic membranes are generally multilayered structures, which are classified based on their pore diameter into microporous, mesoporous, and macroporous.¹⁷ Ceramic membranes are composed of three distinctive layers, namely, alumina support, intermediate layer, and filtration layer. The alumina support was sintered at elevated temperatures (1600 °C or above) to achieve high bending energy to act as a suitable support. Several intermediate layers are incorporated to affectively avoid penetration. The last layer, the membrane layer, is coated to ensure the desired separation intended by the researcher. The main issue that needs immediate attention as far as ceramic membranes are concerned is the high energy required to synthesize alumina support. Due to this very reason, the synthesis of ceramic membranes is cumbersome compared to the polymeric membrane.¹⁸ Nanofiltration was imbibed as an alternative or as an add on for reverse osmosis in water purification. The success rate of NF as a suitable membrane technique in water purification has created inquisitiveness in researchers to focus even more on nonaqueous purification and separation in specific organic solvent nanofiltration. In order to satisfy the criteria of an OSN membrane, the materials should have strong mechanical stability; that is, they must be swelling resistant and must ensure noncompaction behavior of additives synergized with a high selectivity of the polymeric material used. Hence, due to this an amalgamation of inorganic–organic membranes is found to have a promising application in the field of liquid–liquid separation. There are two possibilities of attaining materials of this choice: (i) inorganic materials are grafted on the surface of the polymeric membranes and (ii) in situ modification of organic polymeric materials into the ceramic matrix.

Liquid–liquid separation has emerged as a vital process in product purification, resource recovery, and microfluid operations which presently are the top fields of research.

Hence, organic solvent nanofiltration (OSN), solvent-resistant nanofiltration (SRNF), and porous membranes are different types of organic liquid separation techniques related to membranes that have come to light. Its application ranges from oil refining¹⁹ to the production of fine chemicals.²⁰

The membrane's application in industries goes back to the early 1960s, and ever since then it has been proven useful in various large-scale industrial applications. The main outbreaks in membrane-based technology are (i) membrane material, (ii) membrane structures, and (iii) bulk production of membranes (organic or inorganic materials). To be a self-sustainable and efficient separation technology on a commercial scale, membranes need to accomplish a few criteria such as high flux, enhanced rejection/selectivity, mechanical stability, antifouling ability, temperature resistance, cost efficiency, and the ability to be miniaturized into high surface area modules. Another important characteristic of the membrane is the porosity or the pore distribution, which directly governs the flux and rejection ability of the membrane.²¹ A few of the most commercial membranes used in organic solvent nanofiltration are STARMEM 122, STARMEM 240, DuraMem 500, DuraMem 280, PuraMem S600, PDMS:MPF-44, etc.^{22–26} These listed membranes shown solvent stability in various organic solvents such as methanol, ethanol, acetone, isopropyl alcohol, carbon tetrachloride, etc. Keeping in mind all the above-mentioned points, membranes have an eminent scope in industrialization or commercialization for large-scale application. However, as discussed above, the compromise on either selectivity or permeability is definitely an issue that must be tackled, with which further growth and knowledge on the drawbacks of membrane-based technology can be handled to some extent.

The graph above (Figure 2) expresses the number of publications over a period of two decades (literature data were

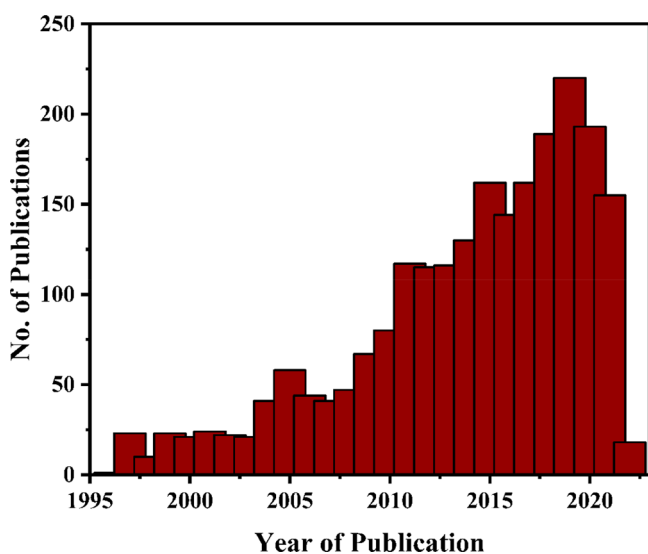


Figure 2. List of publications related to liquid–liquid separation using membranes.

extracted from the Web of Science) in the area of liquid–liquid separations achieved through membranes, void of pervaporation, or any high-energy-consuming separation techniques. Compared to previous articles published by researchers, we hope this review will play a pivotal role in the future research of polymeric membranes used to attain solvent–solvent separa-

tion. The roles of various additives, membrane materials, membrane modifications, and various others factors influencing the membrane's ability are evaluated. This review focuses on research output so far on liquid separation, except conventional types of separation as mentioned before, and we as authors believe membrane technologies involving OSRO and OSN are promising techniques to achieve the desired liquid–liquid separation.

2. TYPES OF ORGANIC SEPARATIONS

The significance of organic chemicals in industries has prompted its extensive investigation in membrane technology. The similar physical characteristics, strong intermolecular interactions, and presence of azeotropes among organic liquids call for membrane separation over other separation techniques.⁴

Organic solvent nanofiltration (OSN) is a promising energy-friendly and waste-efficient process to separate organic moieties to the molecular scale and has embraced the attention of pharmaceutical industries.²⁷ OSN can be amalgamated with other purification techniques for the intensification of yields, purity, and energy efficiency. The heart of OSN is the OSN membrane, which not only should harbor high permeance and high rejection but also must have chemical stability.¹² Membranes used in OSN can be organic or inorganic polymeric materials. The factors which decide the membrane performance are solvent stability, swelling resistance of the membrane, and mechanical, thermal, and chemical stability of the membrane material. In general, it is observed that polymers lose their physical integrity when brought into contact with organic solvents.¹³ The commonly encountered challenges in OSN are inefficient separation leading to low yield or purity and elevated solvent consumption.⁵

2.1. Polar/Nonpolar Separation. A molecule is considered to be polar when two atoms do not share the covalently bonded electrons equally, which eventually leads to one part of the molecule being positively charged and the other part being negatively charged. This phenomenon is found to occur when there is a difference in electronegativity (range 0.5–2.0) between two atoms. However, nonpolar molecules share electrons equally in a covalent bond, and there is no electrical charge across the molecule, as the electrons are equally distributed. The sense of nonpolarity comes into play when the bonded atoms have the same or similar electronegativity.^{28,29} A polyamide selective layer was synthesized over the aliphatic polyketone support to achieve methanol–toluene separation. The precursor molecules used for the synthesis of the selective layer are 1,3,5-benzenetricarbonyl trichloride (TMC) and 1,3-phenylenediamine (MPD), and they were cross-linked via interfacial polymerization on the support. This membrane is found to show a better separation factor when compared to commercial membranes. The organic mixture chosen for separation was methanol and toluene with the ratio of 9:1 with a maximum flux of 8 LMH and a separation factor of 8.4 (Figure 3). The stability of this membrane in organic solvents was calculated using the Hansen solubility parameter difference ($\Delta\delta_p$) (Table 1) of the membrane and the liquid under consideration. Higher $\Delta\delta_p$ accounts for the lower polarity of the solvent tuning the separation to be polarity dependent.⁹

Similarly, another group of researchers was engaged in the separation of organic solvents using RO membranes designated CMS-7, perfluoro-2,2-dimethyl-1,3-dioxale copolymerized with tetrafluoroethylene (PDD-TFE). Various permutations of

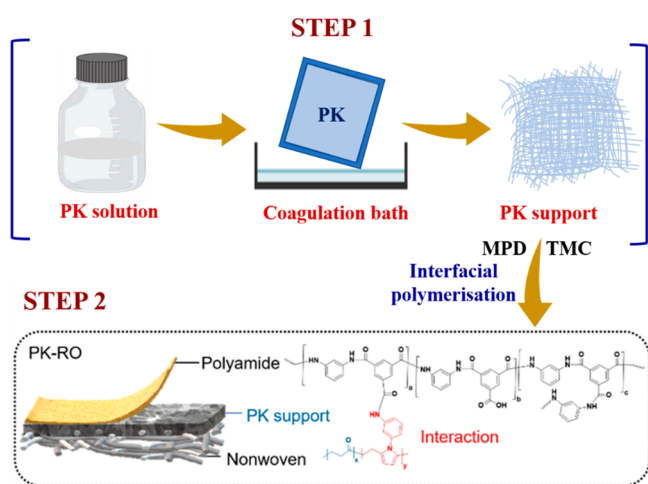


Figure 3. Fabrication of the polyamide membrane and polar liquid model and nonpolar liquid model for separation of polar (methanol)/nonpolar (toluene) mixtures.⁹

Table 1. Hansen Solubility Parameters of a Few Organic Solvents and Their Properties³⁰

Name	Mol. Wt. g/mol	Chemical Structure	Hansen Solubility Parameter (MPa ^{1/2})
Water	18.02		47.8
Methanol	32.04		29.6
Ethanol	46.07		26.5
Tetrahydrofuran	72.11		19.4
Dimethylformamide	73.09		24.8
n-Butanol	74.12		23.1
Dimethylsulphoxide	78.13		26.7
Ethyl acetate	88.11		18.1
Toluene	92.14		18.2
N-methyl-2-pyrrolidone	99.13		22.9
n-heptane	100.21		15.3

organic liquids were chosen to probe the separation efficiency of the membrane for various polar protic, polar aprotic, and nonpolar organic mixtures. From this study, one can conclude that the mechanism that governs the separation is hydrophobicity of the membrane, pore size, and concentration dependence. Concentration dependence is important because when the composition of a particular liquid exceeds in

concentration then even if the other liquid exists the dominating species permeates as the pure species.³⁰ From the above cited literature, it can be observed that for polar–nonpolar separation the membrane matrix must be hydrophobic if the feed consists of a high concentration of nonpolar moieties and hydrophilic for polar moieties. Another important factor is the pore size and pore distribution of the membrane, which can be tuned by using a suitable solvent–nonsolvent during the phase inversion process or even by managing to imbibe additives that meet the needs and tunability of the membrane.

Another class of polar–nonpolar separation is oil–water separation. Although organic liquid–water separations are not considered as an organic liquid separation, some examples are included to showcase the candidature of membranes (Table 2).

Table 2. List of a Few Membrane Materials Used for Liquid–Liquid Separation

Sl. no.	Membrane	Solvent system	Polarity	Ref
1.	Aliphatic polyketone supported polyamide (PK-RO)	• Methanol–toluene	Polar–nonpolar	9
2.	Perfluoro-2,2-dimethyl-1,3-dioxane copolymerized with tetrafluoroethylene	• NMP–toluene • (DMF)–toluene • DMSO–toluene	Polar–nonpolar	30
3.	Polyamide membrane manufactured from copolymers of diaminophenylindane with benzophenone tetracarboxylic dianhydride	• lube oil–water	Polar–nonpolar	32
4.	Graphene oxide–polyether sulfone	• Oil–water	Polar–nonpolar	33
5.	Graphene oxide (GO) based laminated membrane	• Ethanol–water	Polar–polar	2

Oil pollution has contributed to a major environmental hazard, which is a hurdle for the expansion of petroleum production. The current methods used for the treatment of oil spills include blooms, skimming, and burning of oil which can gradually increase the concentration of carbon dioxide in the environment.³¹ Polyamide membranes manufactured from copolymerization of diaminophenylindane with benzophenone tetracarboxylic dianhydride showed excellent chemical resistance and economically viable flux and high rejection (99%) of aliphatic hydrocarbon from lube oil filtrates at 14 °C.³² Another group synthesized a graphene oxide–polyether sulfone (GO-PES) hollow fiber and flat sheet membrane for oil–water separation. The dope compositions of GO in both the flat sheet (FS) and the hollow fiber (HF) membranes were the same, but the morphology and pore size showed variance due to the fabrication. The HF membranes showed higher oil rejection (~99%) unlike FS membranes (up to 50%) and accounted for the small pores in FS membranes, wherein the permeation flux is also maintained due to enhanced flow dynamics.³³

The use of membranes for the treatment of oil spills is one possibility. These separation techniques endow nanocomposite membranes and surface-modified membranes with a class of membranes that are hydrophilic/oleophobic, which retain oil and enable passage of water, and a second class of membranes which have hydrophobic/oleophilic behavior which removes oil by adsorption by the use of silica aerogels, metal-coated

membranes with polydimethylsiloxanes (PDMS), or polytetrafluoroethylene (PTFE).³⁴

When the structure of water/alcohol or water/organic liquid is spherically designed, hydrophilic membranes are of interest. Thereby, diffusion of water molecules into the membrane during separation can be expected. In order to facilitate the diffusion of water molecules through the membranes, dissociation groups are incorporated into the membrane matrix to raise the affinity of the membrane. One such material is a chitosan acetate (ChitoA) moiety which is found to have amino and hydroxyl groups which render resistance against organic solvent and enhance hydrophilicity.³⁵ Though there have been many advances made in oil/water separation, most of the material still meets the demands of practical applications. Future development must mainly focus on cost-effective, environmentally friendly, and reusable materials with high scalability. The major impediment witnessed in oil–water separation is the fouling behavior of oil due to the hydrophobicity of oil used. One must always strive to attain a high flux recovery ratio (FRR) and a long shelf life of the membrane irrespective of the separation intended.

2.2. Nonpolar/Nonpolar Separation. BTX, abbreviated as benzene, toluene, and xylene, are the primary raw materials for petrochemicals. The consumption of xylene isomers is of unbalanced proportion, and *p*-xylene (*pX*) is also found to be valuable and is used in the synthesis of polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). *o*-Xylene is used in the production of phthalic anhydride, and *m*-xylene is used in the synthesis of isophthalic acid.^{36,37} Xylene in general is derived from crude petroleum and found to have application in tissue staining, as a lubricant in motor and oil break fluids, in paint thinners, etc.³⁸ Xylene as we all know exists in three isomeric forms derived from catalytic reforming of crude oil. All three forms *o*-xylene (*oX*), *p*-xylene (*pX*), and *m*-xylene (*mX*) have different applications with respect to each other. *p*-Xylene acts as a precursor in the synthesis of a polymer, polyethylene terephthalate, which in turn is used in food packing, clothing, and household fabrics,^{39,36} and these isomers are challenging to separate due to their similar molecular mass and physical properties (boiling point of *pX* 138.38 °C, *mX* 139.19 °C). Use of membrane technology to achieve separation of the isomeric mixture is still a field unventured and still remains a future scope. One such group synthesized novel dense composite membranes made of polyhexylmethylsiloxane (PHexMS), polyoctylmethylsiloxane (POMS), and polydecylmethylsiloxane (PDecMS) for the separation of saturated and unsaturated hydrocarbons. Polydimethylsiloxane (PDMS) was used for comparison. On increasing the alkyl chain length from hexyl to decyl the selectivity for *n*-butane/methane gas increases from 15.5 to 18.2 which is greater than the separation factor exhibited for PDMS (7.6), but permeabilities of the gas are found to drop with an increase in carbon chain length. A phenomenal decrease in separation factor was observed in these gas mixtures when compared to ideal gases due to butane, causing membrane swelling.⁴⁰ When species are of the same polarity or are isomeric in nature, the separation process can be achieved only by amending the pore size of the membrane or by certain modifications on the membrane surface such that only a particular isomer can easily diffuse through the matrix.

2.3. Polar/Polar Separation. Ethanol/water separation is found to be one of the most demanding and stimulating separations in azeotrope mixtures and if solved will definitely

create a breakthrough in membrane technology. Ethanol specifically is one of the most clean and sustainable sources because of its renewable, economic, and environmental properties.¹³ Zhan et al. used graphene oxide (GO) based laminated membranes for the separation of liquid solvents. Herein the solvation aspect of layered GO materials was found to be their trademark property due to the hydrophilicity of GO. There exists a molecular competitive insertion of mixed solvents when they permeate through the GO interlayer pore, and the swelling nature becomes more complicated. For a GO concentration of 7–10% having a pore size of 7 Å, both ethanol and water were able to spontaneously diffuse through the pores, but the rate of permeation of ethanol is greater than water as it takes ~100 ns for ethanol to attain a relatively stable intercalation. It is noted that the number of water molecules occupying the pores is greater than ethanol, with increasing oxidation degree of GO (7–20% and 7–35%). GO with 7–35% showed a higher amount of water with only a few ethanol insertions. The reason for this trend is the repulsion of the functional groups GO and ethanol at the GO nanochannels. It was also observed that water molecules were sparsely distributed in the slit-like pores due to the obstruction effect of ethanol molecules at the pore entrance. For GO with a pore size of 9–12 Å, the nanochannels can be intercalated simultaneously by both ethanol and water. Ethanol molecules are found to penetrate into the pores compared to water molecules due to the strong surface affinity of the first with the GO surface. Therefore, the average dwelling time for ethanol at the GO surface is relatively more than that of water, inferring that ethanol molecules can reside better compared to water on the GO surface.³⁸ Very limited research has been done on polymeric membranes to achieve alcohol–water separation due to their closely related size and polarity.

Bioethanol has been found to be a good source of biofuel and is environmentally benign. However, the glitch is that ethanol does not come pure but with a few traces of water and other small alcohols that hamper the purity and efficacy of ethanol required. Tang's group synthesized poly(*N*-isopropylacrylamide) (PNIPAM) along with a 5-coordinate zinc-based metal–organic framework designated as the DMOF composite. A pristine MOF was not used as such due to its lability in a water medium, whereas the DMOF–PNIPAM composite was water inert, prevented MOF decomposition, and tuned the hydrophobicity and pore size of the membrane with a different dosage of PNIPAM. This is because of the amide group present in the PNIPAM, which absorbs moisture which in turn protects the MOF from water degradation. It was observed that the separation factor increased with an increase in applied pressure: i.e., for methanol–ethanol 3.5 to 17.3 and for water–ethanol an increment from 2.1 to 3.3 were observed.⁴¹

3. MODELS PROPOSED FOR THE TRANSPORTATION OF SOLVENT MOLECULES ACROSS THE MEMBRANE MATRIX

3.1. Solution Diffusion (SD) and Pore Flow (PF) Models. The transport of organic molecules across OSN membranes is interpreted using solution diffusion (SD) and pore flow (PF) models. The article published by See-Toh and his group gives more importance to the PF mechanism because of its usefulness in explaining the effects of changing dope composition on the membrane filtration performance. MWCO studies alone are insufficient to explain the membrane's ability to discriminate between separating species. Michael and his

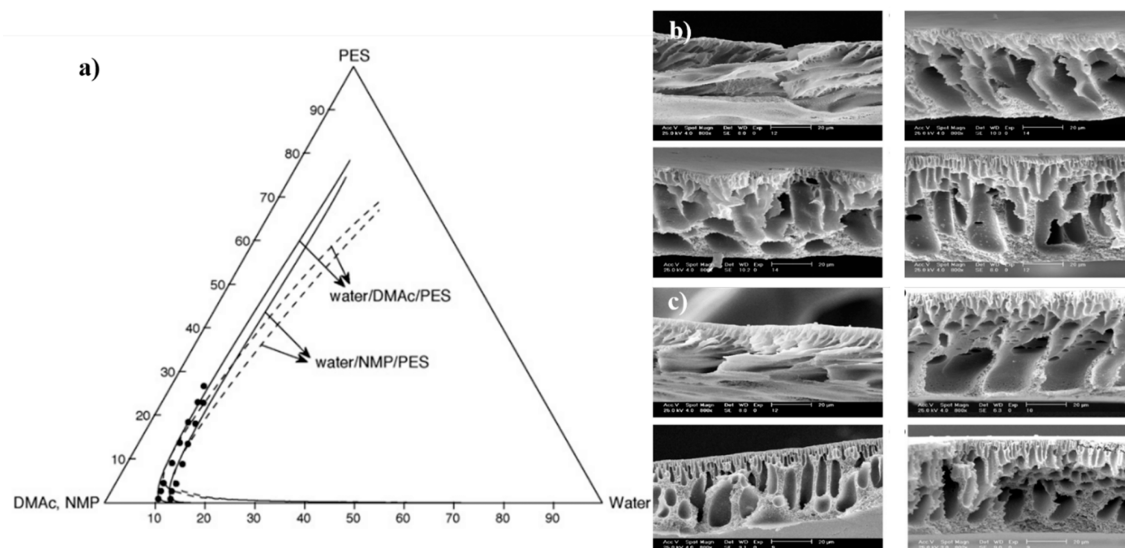


Figure 4. (a) Schematic representation of theoretical binodal and spinodal curves for water/DMAc/PES and water/NMP/PES systems. The dotted plot represents the experimental cloud point. Cross-sectional SEM images of membranes prepared from (b) NMP/PES solutions coagulated in water with an increase in polymer solution concentration and (c) membranes prepared from DMAc/PES solutions coagulated in water with an increase in polymer solution concentration, respectively.⁴⁵ Reprinted with permission from [Soroko, I.; Lopes, M. P.; Livingston, A. The Effect of Membrane Formation Parameters on Performance of Polyimide Membranes for Organic Solvent Nanofiltration (OSN): Part A. Effect of Polymer/Solvent/Non-Solvent System Choice. *J. Memb. Sci.* 2011, 381 (1–2), 152–162. [10.1016/j.memsci.2011.07.027](https://doi.org/10.1016/j.memsci.2011.07.027)]. Copyright 2008 Elsevier.

group suggested the use of two-parameter log-normal distributions of sieving characteristics of various membranes. Herein, the mean solute diameter (d_s) and solute standard deviation (σ_s) were used to explain the size range and rejection of solutes by different membranes.

The rejection R_f can be explained by the below equation

$$R_f = \text{erf}(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^z e^{-u^2/2} du \quad (1)$$

The solution-diffusion model was first proposed in the 19th century for transportation across dense membranes but was not widely accepted until the 1970s. According to the solution-diffusion model, dissolution/sorption causes permeation of molecules through the membrane toward the permeate side. Dissolution/sorption behavior and the difference in rate of diffusion are the motive for separation of molecules across the membrane.

This model is found to have applications in all types of dense membranes ranging from gas separation, pervaporation, and dialysis to RO membranes. The main pillar of the theory is that the driving force for species to permeate across the membranes is due to the gradient in chemical potential (a form of thermodynamical potential), which can be simplified as

$$J_i = -c_i D_{i,p} \frac{d(\ln \gamma_i)}{dx} + \frac{c_i D_{i,p}}{RT} V_i \frac{dp}{dx} - K_{i,d} D_{i,\infty} \frac{dc_i}{dx} - \frac{\gamma_i c_i D_{i,p}}{RT} F \frac{d\Psi}{dx} + K_{i,c} c_i V \quad (2)$$

where J_i = flux of component i (either a solvent or a solute) through the membrane; c_i = (electro)chemical potential of component i ; x = membrane position; and D_i = proportionality coefficient linking the chemical potential gradient to the flux. The fame and wide use of the SD model is due to the membrane driving forces such as gradients in temperature, electromotive force, concentration, and pressure.⁴²

4. THEORY BEHIND THE PORE FORMATION MECHANISM

Asymmetric membranes for OSN are usually prepared by a phase inversion process, and a polymeric dope solution undergoes transformation from the liquid to solid state. This process is initiated by liquid–liquid demixing. A thermodynamically unstable solution is separated into two phases, i.e., the polymer-rich phase and polymer-lean phase, to reach thermodynamic stability.⁴³ The phase inversion method is usually employed in the synthesis of asymmetric membranes, where the casting solution consists of the polymer dissolved in a suitable solvent. Later, the membrane is cast and immersed in a nonsolvent coagulation bath. It is in this step where exchange of solvents and nonsolvents occurs and eventually leads to pore formation. The principle of the pore formation process contains both thermodynamics of the ternary diagram and mass transfer properties.⁴⁴ The solvent and nonsolvent ratio along with the choice of polymer and its concentration and evaporation period have been found to have a great influence on the molecular weight cutoff (MWCO) and flux. The figure below (Figure 4a) is a suitable figure for the ternary phase diagram which depicts a three-component system comprised of a polymer, a solvent, and a nonsolvent which is commonly used in membrane fabrication by nonsolvent-induced phase separation (NIPS). Presently, most of the polymeric membranes are synthesized via the phase separation (phase inversion) method. This technique involves two phases: a solid phase that is rich in polymer which eventually forms the membrane matrix and a liquid phase that forms the membrane pores. The phase separation can be achieved by nonsolvent-induced phase separation (NIPS), thermally induced phase separation (TIPS), vapor-induced phase separation (VIPS), and evaporation-induced phase separation (EIPS). Compared to the listed phase separation techniques, NIPS is mostly preferred for the synthesis of polymeric membranes. In the NIPS method, a homogeneous polymer solution is casted onto

Table 3. List of MOFs and ZIFs Used for OSN

Sl. no.	MOF	Metal	Ligand	Window size	Ref
1.	HKUST-1	Cu	1,2,4-benzenetricarboxylic anhydride	0.9 nm	52
2.	mZIF-8	Zn	2-methyl imidazole	0.64–0.74 nm	53
3.	MIL-1019(Cr)	Cr	terephthalic acid	1.2–1.6 nm	54
4.	MIL-1019(Al)	Al	terephthalic acid	0.6–0.64 nm	54
5.	ZIF-11	Zn	benzimidazole	0.3 nm	54
6.	ZIF-67	Co	2-methyl imidazole	3.43 Å	55
7.	UiO-66 NH ₂	Zr	2-amino terephthalic	0.89	56

a thin film or spun in the case of a hollow fiber membrane, after which the cast is immersed in a coagulation bath (mostly water).

The theoretical binodal and spinodal curves for water/DMAc/PES and water/NMP/PES are represented in Figure 4a. This was plotted based on the Flory–Huggins theory of polymeric solution and the binary interaction parameters that were determined. The theoretical data were confirmed by carrying out cloud point titration. The above binodal curve for water/DMAc/PES is closer to the polymer–solvent axis; therefore, less water is required for precipitation of PES in this system. From the cross-sectional images of the membranes prepared from water/DMAc/PES and water/NMP/PES, it is observed that the sublayer of all the images consists of microvoids. This proves high affinity and interaction between water and the solvents in the system which is supported by the interaction parameters of water/NMP and water/DMAc pairs. It was found that membranes with irregular morphology are not considered to have efficient mechanical strength. With an increase in polymer concentration, the morphology changes to regular ore channels with closed ends. With a further increase in polymer concentration, channel-like structure diminishes, giving rise to a sponge-like structure in the membrane and eventually leading to tear-like pore structures (Figure 4b).⁴⁵

5. ADDITIVES USED IN OSN AND SRNF

5.1. Metal–Organic Framework (MOF) and Zeolite–Imidazolate Framework (ZIF).

MOFs are those moieties which are composed of metal ions which are present in the cavity encapsulated by organic ligand bridges. These molecules are found to have a plethora of applications ranging from medicines⁴⁶ to separation and purification.⁴⁷ The tunable pore structure which could be used to substitute various metal ions based on the metal's ionic radius extends its use, along with the organic bridges where the linker molecules and the chains can be altered depending on the intended application. Further, to enhance the durability and functionality of the MOFs, recently bimetallic MOFs have been designed. Based on a literature survey one can say that the distribution of the metal ions in a bimetallic MOF can be categorized into “core–shell” and “solid solution structures”. From the figure, one can conclude that for membrane application solid solution MOFs are suitable candidates due to the vacancies or voids present in the structure which could in turn aid researchers to achieve the desired separation.⁴⁸ MOFs were initially used for gas separation and storage due to their extensive properties. Therefore, the area of liquid–liquid separation aided by MOFs is still adequately exploited. There are two ways in which the MOF can be utilized for liquid–liquid separation: (i) utilizing the MOF as such without any polymeric additive and (ii) using the MOF as an additive in the polymeric matrix to enhance the physicochemical properties of the material. The second type is

found to be most commonly used for water separation and purification if and only if MOFs have thermodynamic and kinetic stability which is dependent on the free energy of hydrolysis of the MOF and activation energy barrier, respectively. Of the usual methods used, oily wastewater treatment is commonly employed due to the high permeability and selectivity behavior of MOFs toward water. The mechanism through which separation of oil from water is achieved is either by hydrophilicity or size-exclusion theory.⁴⁹ Since metal–ligand bonds are labile as observed in earlier studies,⁵⁰ water-inert MOFs with strong thermodynamic and kinetic stability are preferred. Water-stable MOFs are divided into three categories: (i) Carboxylated organic framework encapsulating high valence metal ions, which are prone to be less susceptible to water. (ii) Metal azolate frameworks, which consist of nitrogen donor ligands. These types of ligands are found to be water stable, rationalized by the HSAB principle. Since nitrogen-donor azolate ligands are soft bases, they are likely to interact with softer divalent metal ions, resulting in stronger MOFs. (iii) The last class of water-stable MOFs are MOFs with a hydrophobic pore or metal blocked MOFs with specialized steric hindered nature to achieve stability in an aqueous medium.⁵¹ Table 3 gives insight into various MOFs used for organic solvent nanofiltration. Though there are a limited number of MOFs used in OSN, they can be tuned based on our need. The counterion and ligand can be substituted with other ions and ligands having seamless combinations depending on the types of separation (mentioned in Section 2). MOFs are one class of solid crystalline materials with a plethora of functionalities, and the functional groups present on MOFs can be metamorphosed based on the researchers' criteria. Table 3 gives different types of MOFs and ZIFs used in OSN. From this table, one can conclude that MOF-based membranes have a high potential in liquid–liquid separation. Although the mentioned MOFs in the table are found to have strong solvent stability and suitable candidature, they have not yet been used for liquid–liquid separation. Based on the window size offered by the material, one can accordingly pick a suitable MOF or ZIF depending on the size of the organic species they intend to separate (Figure 5).

Zeolite imidazolium frameworks are another class of nanoporous materials with high thermal and chemical stability. This is because membranes pave the way for ZIF's application in organic solvent separation. These materials are found to have tetrahedral metal clusters with an imidazolate ligand system. The pore size of ZIFs can be tuned by altering the type of imidazolate ligand used. Zeolite-derived materials have the ability to increase permeation even without affecting the rejection performance of the membrane, and the functionalization of zeolites is relatively easy. Namvar-Mahboub and coworkers prepared UZM-5/polyamide TFC nanocomposite membranes to study the extent of oil rejection by membranes

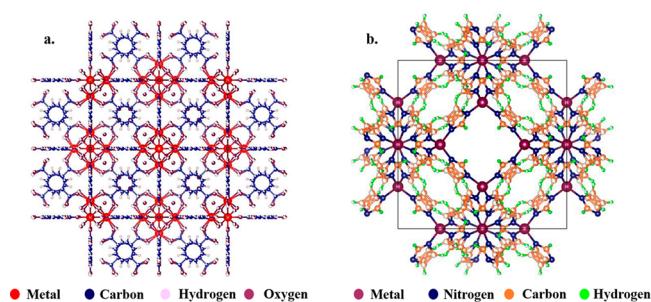


Figure 5. Crystallographic images of (a) UiO-66 MOF and (b) ZIF-8.

in methyl ethyl ketone and toluene as the solvent medium. The extent of oil rejection is found to increase with an increase in zeolite concentration, which is attributed to the solvent channels created by zeolite which enhances the solvent transportation rate, thereby increasing the concentration of MEK and toluene in permeate and decreasing the oil concentration in the permeate. On increasing the dosage of zeolite in the membrane, agglomeration of zeolite generates nonselective voids, leading to diminished selectivity. The pore diameter of UZM-5 is 16.8 Å, which is less than the kinetic diameter of MEK and toluene, 6.1 and 5.2 Å, respectively.⁵⁷ In this section, we have discussed a few ceramic materials used in OSN which are found to have tunable features such as altering their ligand system and adding an additive within the pores that alters their functionality, etc. Due to this, natural zeolites and MOFs are found to be suitable aspirants for OSN.

5.2. Inorganic and Carbon-Based Fillers. Assimilation of inorganic fillers inside the membrane matrix exhibits thermal stability, mechanical stability, and chemical inertness of the composite membrane which is useful for its application in organic solvent filtration. Silica, titania, inorganic nanoparticles, etc., are few additives that have proven their candidature in OSN. Silica, being hydrophilic in nature, has attracted researchers for its use as a nanofiller. Pakizeh and Mahboub functionalized silica particles using aminopropyltriethoxymethylsilane (APDEMS) as the silane coupling agent and procured amino-functionalized nanoparticles that were used as a filler for lube oil separation from methyl ether ketone (MEK) and toluene with a rejection efficiency of 94.72%.⁵⁸ In another study, Wang's group fabricated a few functionalized silica nanoparticles (spheres) as membrane additives for solute–solvent separation which can be used as hydrophobic and hydrophilic fillers depending on the functionalization achieved. The membrane material showed high ethanol flux of up to 30.8 LMH on using hydrophilic silica spheres and a hexane flux of 21.7 LMH on using hydrophobic silica spheres as the membrane additive.⁵⁹ Another important inorganic material that is used in membranes for organic solvent

separation is carbon-based material such as graphene oxide, reduced graphene oxide, graphene quantum dots, etc. These carbon-based materials have especially graphitic type material which has a major scope in membrane technology because of its single atom thick layer and multichannels provided in the matrix, which enhance solvent permeability. Future fabrication of GO is done in order to enhance the stability and functionality of GO in the membrane application. The addition of functionalities such as $-\text{NH}_2$, $-\text{OH}$, $-\text{COOH}$, and GO tend to the probability of imbibing GO in OSN or SRNF membranes. Low flux and high solvent resistance being a major issue, Goa's group used polyimide membranes decorated by graphene quantum dots (GQD) in various dosages with high flux and solvent resistance ability in ethanol and dimethyl formamide (DMF). Similarly, another group used amino-functionalized GQDs, which showed even higher permeance for the same solvents and separation ability than the previous report where they used unfunctionalized GQDs.^{60–62} Gao's group used GQDs but altered the polymeric support to polyethyleneimine and proved superior organic solvent resistance for 81 days at room temperature and 45 days at 80 °C for DMF solvent. Another group of researchers used octadecylamine-functionalized reduced graphene oxide, using polyamide as the polymeric support, and fabricated the membrane by interfacial polymerization. This membrane should have high permeance toward ethanol, and separation occurs through diffusion along selective gaps in the membrane matrix.^{63,64} From the above survey (including Table 4) on inorganic and carbon-based fillers, we can suggest that 2D sheet-like materials still have tremendous application in the field of liquid–liquid separation. Though all the literature cited focused only on stability, their reproducibility and role in solvent–solvent separation are still left unventured. These materials are found to have tunable features and are also easy to functionalize depending on the set objective.

6. FOULING AND ANTIFOULING

Fouling is the accumulation of undesired components on the membrane surface or inside the membrane pores.⁶⁶ The reduction in membrane performance is due to either buildup of a secondary layer or failure of the existing layer's performance. Usually, it is observed that membrane cleaning is easier if deposition occurs at the membrane–feed interface (in the front of the membrane). This can be overcome by simple modification in the outer surface, e.g., separation of negatively charged biomolecules at neutral pH using a negatively charged membrane.³ Ever since membrane technology was developed, fouling has been the bottleneck of membrane separation which hinders the membrane's performance. In general, there exist two main fouling-defense mechanisms for ultrafiltration (UF) membranes: (i) fouling-resistant mechanism which demands

Table 4. Inorganic Additives Used in Organic Solvent Nanofiltration

Sl. no.	Additive	Support layer	Solvent	Flux	Ref
1.	WS ₂	Polyacrylo nitrile	Ethanol	43.35 LMH	65
2.	Amino-functionalized SiO ₂	Poly(ether imide)	Methyl ether ketone and toluene	10.4 LMH	58
3.	Functionalized SiO ₂	Poly(ether imide)	Ethanol and <i>n</i> -heptane	30.8 LMH and 21.7 LMH	59
4.	Graphene quantum dots (GQDs)	Polyimide	DMF and ethanol	18.3 LMH and 22.6 LMH	60
5.	Amino-functionalized GQD	Polyimide	DMF and ethanol	38 LMH and 41LMH	62
6.	GQD	Polyethylenimine	DMF	40.3 LMH	63
7.	Functionalized reduced graphene	Polyamide	Ethanol	6.0 LMH	64

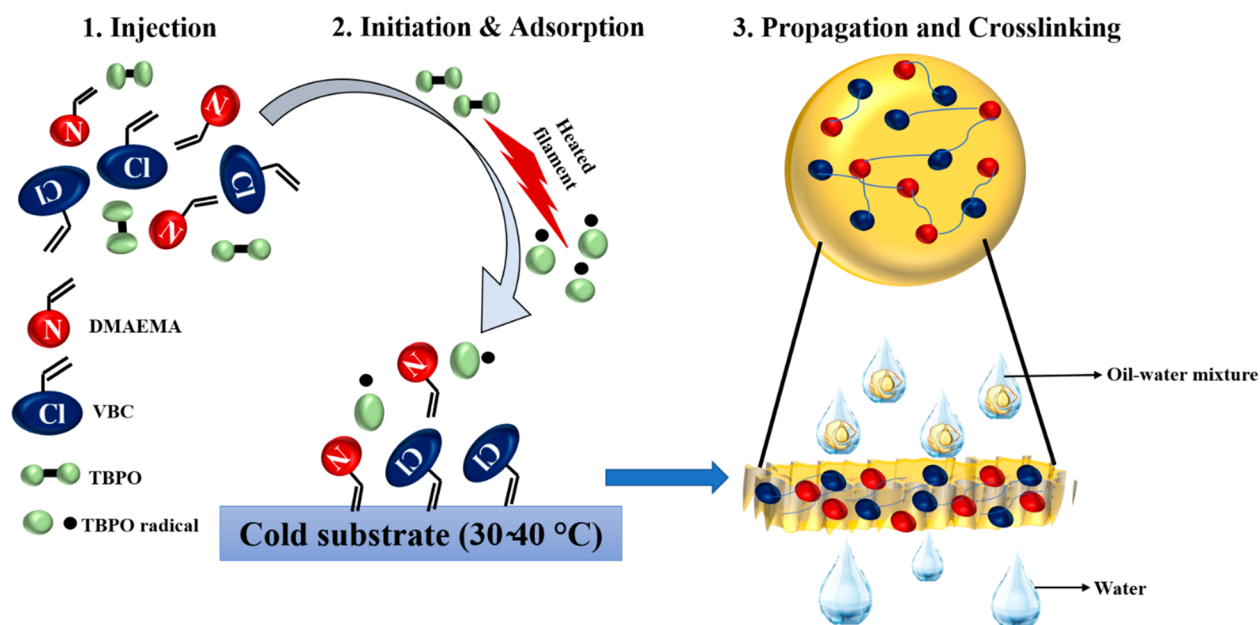


Figure 6. Schematic representation of chemical vapor deposition used in the synthesis of cross-linked ionic polymers for oil–water separation.⁷⁰

hydrophilic modification, leading to the formation of a compact hydration layer preventing the approach of organic pollutants and (ii) fouling release mechanism which consists of low-energy perfluorinate groups which have the tendency to weaken the interfacial bonds of organic pollutants and membranes which in turn enable easy removal of organic foul under minimum stress. It is evident that a UF membrane with a synergistic effect of both the mechanisms is best suited.⁶⁷ In microporous membranes (UF and microfiltration–MF membranes), fouling usually occurs by pore blocking, solute adsorption, and cake/gel layer formation.⁶⁸ While talking about RO membranes, it is found that this class of membranes does not have dense distinct pores and is rather dense in nature. Therefore, RO membranes are susceptible to surface fouling. The major class of foulants is suspended particulate matter, dissolved organic substances, dissolved proteins, and biological matter. Due to the repulsive forces of the electrical double layer, the suspended solids remain suspended in the medium, but when attraction forces (van der Waals forces) overpower the suspended particles, the particles become unstable and form agglomerates. Amiri and Samiei in their work stated that carbon-based feeds like oil, cationic surfactants, plant materials, etc., are found to have more attraction toward the membranes. Another type of fouling is observed in the case of biological samples where the cells gather and get stuck on the membrane surface, forming a biofilm that eventually hinders permeate flux across the membrane.⁶⁹ Similarly, another group proposed two enhancements of the existing model using a hollow fiber membrane, one of which was taking into consideration the adhesive forces between particles and the membrane surface which have an influence on the cake formation layer and back-flushing efficiency. The other enhancement is monitoring the decisive influence of particle and membrane pore size distribution on cake formation and pore blocking [fouling]. It is also a known fact that fouling is inevitable and eventually leads to high operating pressure, flux decline, and frequent chemical cleaning and reduces membrane life.⁶⁶ Fouling mitigation has always been challenging as far as reproducibility and recyclability are

concerned. Various modifications on the membranes either by ex situ or in situ modification must be imbued to enhance the shelf life of the membrane. Other ways to overcome this hurdle are to eliminate the foulant by washing methods without disturbing the membrane's mechanical and physicochemical properties.

7. SURFACE MODIFICATION FOR ENHANCED MEMBRANE PERFORMANCE

A variety of surface modifications have been done with the objective of improving the surface properties of the membrane to enhance the performance. Surface modification in membrane technology can be classified in two ways, physical and chemical methods, depending on the interaction between the membrane surface and the activating agent. Techniques such as grafting, coating, chemical coupling, plasma treatment, and chemical vapor deposition (CVD) are few of the versatile techniques employed to achieve antifouling/antimicrobial RO membranes.⁶⁸ Initiated chemical vapor deposition utilizes a radical polymerization reaction to develop polymeric thin film from vapor-phase monomers and a radical initiator. The injected monomers are adsorbed onto the substrate's surface, while formed free radicals are delivered onto the adsorbed monomers. Eventually a polymer thin film which is free of dewetting is synthesized.⁷⁰

Grafting is a technique where macromolecules and surface-modifying polymers are anchored on the membrane surface. Grafting can be achieved by either a grafting-from or grafting-to approach. Grafting can be classified based on the technique for surface modification employed, such as cationic, anionic, free radical, redox, ultraviolet (UV), plasma, enzymatic, CVD, and atom transfer radical polymerization (ATRP). The chain length and grafting density can be controlled by meticulous grafting.⁶⁸ Compared to the above-mentioned techniques, UV radiation (Figure:6) is found to have the upper hand as the wavelength can be adjusted selectively depending on the reaction under consideration, and undesired reactions can be avoided.

The grafting reaction can be divided into two groups: grafting-to and grafting-from. In grafting-to reactions, there is direct coupling on the reactive group or end group of the membrane surface, e.g., introduction of amino, aldehyde, epoxide, etc. This type of grafting reaction is usually done to functionalize UF or MF membranes. Grafting-to is achieved by taking monomers of acrylates or acrylamides, etc., in either aqueous or organic solution and later polymerized by a radical route by controlling the termination reaction. Reactive coating is another method where a polymer is coated on the membrane surface via in situ synthesis by either adsorption/adhesion or interpenetration, that is, mixing the functional material and the base polymer in an interphase.⁶ Reversible addition–fragmentation chain transfer (RAFT) is a versatile technique used to modify the surface of UF and RO membranes. This approach is found to control the size of the polymers to synthesize macromolecular architectures such as block, gradient, statistical comb, brush, star, hyperbranched, and network vinyl copolymers under the existing polymerization conditions. This technique is found to be handy in the synthesis of end-functionalized polymers to modify surfaces of polyamide RO membranes.⁷¹ The hydrophilicity of RO membranes and the hydrophobicity of the NF membranes are determined by the permeation properties of alcohols and alkanes. It is found that the permeability of polar solvents is 8–10 times more than nonpolar solvents in hydrophilic membranes, and in the case of hydrophobic membranes the permeability of the nonpolar solvent is 2–4 times greater than the permeability of polar solvents. A study carried out by Van Gestel et al. showed that the surface modification of membranes with high molecular weight silanes (C8 silane) increases the permeability of *n*-hexane to a greater extent compared to lower molecular weight silanes. This trend was observed due to the formation of more hydrophobic pores with high affinity toward *n*-hexane and cyclohexane by attachment of long chains of alkyl groups to the walls of the pores. Sun et al. proved that addition of triethylamine (TEA) and camphor sulfonic acid (CSA) into the *m*-phenylenediamine (MPD) solution during the process of interfacial polymerization enhanced the roughness of the synthesized polyamide membrane along with an increase in surface roughness with a gradual increase in membrane flux, but there always lies a trade-off relationship between the surface area and the fouling ability of the membranes with an increase in surface roughness.

The integrally skinned asymmetric membrane is the only type of asymmetric membranes used in OSN. These membranes are prepared via the phase inversion (discussed in section 5) method developed by Loeb and Sourirajan. Another type of asymmetric membranes are thin-film composite membranes (TFC) which consist of a separating layer on top of a porous substrate. Usually plasma-induced techniques and grafting are well established for obtaining an ultrathin dense skin layer.⁷² Plasma treatment focuses on the interaction with excited atomic, molecular, ionic, and radical species. This technique includes plasma sputtering, etching, implantation, and spraying. This process is achieved by elastic and inelastic collision between materials on the membrane surface and the atoms or molecules activated by inert gases, and the exchange of material is what gives rise to active radicals on the membrane surface (by abstraction of hydrogen from the membrane) which in turn combine with a simple radical in the plasma like oxygen or nitrogen to generate a polymer chain. Plasma gas generated from chloroform and carbon tetra-

chloride enhances the hydrophilicity of the membrane, as it is found that the hydrophilic surface displays higher permeability and reproducibility than hydrophobic membrane surfaces.⁷³

8. CONCLUSION AND PERSPECTIVES

Ever since membrane technology has come into existence, its application is interdisciplinary and fast growing with tremendous improvements. Membranes are purely intended for large-scale applications, but industries hesitate to switch from already existing protocols to membrane-assisted separation, though the latter is economically advantageous. Since it is capital-intensive and the risk of installation is high even though the performance of membranes is good enough, other factors need to be taken under consideration. Use of conventional methods for the separation of organic liquids must be substituted by membranes in order to overcome the energy crisis. Various membrane separation techniques such as OSN and OSRO need in-depth knowledge supported by other theories which enhance the face value of membrane-aided liquid–liquid separation. Membrane fabrication and the synthesis of materials are a continuous process whose challenge is to meet high selectivity, high flux, long-term stability, and organic solvent lability. A membrane matrix with high porosity and elevated solvent wettability also tunes the membrane's ability to uptake solvent molecules and permeate them through the membrane. Even with high solvent uptake, aspect membranes must have long durability in harsh environments, making them apt for long-term studies. Though the inorganic additives are found to be stable and inert in an organic medium, there always lies a trade-off between the selectivity and permeability along with inadequate knowledge of fouling mitigation. Organic liquids in specific are found to imperil membrane morphology; therefore, the development of solvent-stable membranes or solvent-resistant membranes is still a challenge for many membrane scientists. The choice of tailored material and type of surface modification is a top priority to achieve the desired separation, and upscaling the synthesized membrane along with cost efficiency enhances the scope of the membrane. Based on the discussions covered in this review, it is also important to keep in mind the environmental hazards caused due to buildup of these polymeric materials used for separation as they are non-biodegradable. Therefore, substitution of these materials with biodegradable polymeric materials or biomimetic polymeric materials keeping up the promises of artificial polymers could be a great discovery and help in both science and nature.

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Notes

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REFERENCES

- (1) Solvents and sustainability | Feature | Chemistry World. <https://www.chemistryworld.com/features/solvents-and-sustainability/3008751.article> (accessed 2021-05-30).
- (2) Nie, L.; Goh, K.; Wang, Y.; Lee, J.; Huang, Y.; Enis Karahan, H. E.; Zhou, K.; Guiver, M. D.; Bae, T. H. Realizing Small-Flake Graphene Oxide Membranes for Ultrafast Size-Dependent Organic Solvent Nanofiltration. *Sci. Adv.* **2020**, *6* (17), 1–13.
- (3) Joshi, D. R.; Adhikari, N. An Overview on Common Organic Solvents and Their Toxicity. *J. Pharm. Res. Int.* **2019**, *28* (3), 1–18.
- (4) Liu, C.; Dong, G.; Tsuru, T.; Matsuyama, H. Organic Solvent Reverse Osmosis Membranes for Organic Liquid Mixture Separation: A Review. *J. Membr. Sci.* **2021**, *620*, 118882.
- (5) Marchetti, P.; Jimenez Solomon, M. F.; Szekely, G.; Livingston, A. G. Molecular Separation with Organic Solvent Nanofiltration: A Critical Review. *Chem. Rev.* **2014**, *114* (21), 10735–10806.
- (6) Ulbricht, M. Advanced Functional Polymer Membranes. *Polymer (Guildf)*. **2006**, *47* (7), 2217–2262.
- (7) Goh, K. S.; Chong, J. Y.; Chen, Y.; Fang, W.; Bae, T. H.; Wang, R. Thin-Film Composite Hollow Fibre Membrane for Low Pressure Organic Solvent Nanofiltration. *J. Membr. Sci.* **2020**, *597*, 117760.
- (8) Saki, S.; Uzal, N. Preparation and Characterization of PSF/PEI/CaCO₃ Nanocomposite Membranes for Oil/Water Separation. *Environ. Sci. Pollut. Res.* **2018**, *25* (25), 25315–25326.
- (9) Liu, C.; Takagi, R.; Shintani, T.; Cheng, L.; Tung, K. L.; Matsuyama, H. Organic Liquid Mixture Separation Using an Aliphatic Polyketone-Supported Polyamide Organic Solvent Reverse Osmosis (OSRO) Membrane. *ACS Appl. Mater. Interfaces* **2020**, *12* (6), 7586–7594.
- (10) Naik, N. S.; Padaki, M.; Déon, S.; Karunakaran, G.; Dizge, N.; Saxena, M. The Efficient Mixed Matrix Antifouling Membrane for Surfactant Stabilized Oil-in-Water Nanoemulsion Separation. *J. Water Process Eng.* **2019**, *32* (July), 100959.
- (11) Sherugar, P.; Padaki, M.; Naik, N. S.; George, S. D.; Murthy, D. H. K. Biomass-Derived Versatile Activated Carbon Removes Both Heavy Metals and Dye Molecules from Wastewater with near-Unity Efficiency: Mechanism and Kinetics. *Chemosphere* **2022**, *287* (P2), 132085.
- (12) Asad, A.; Sameoto, D.; Sadrzadeh, M. *Overview of Membrane Technology*; Elsevier Inc., 2019. DOI: 10.1016/B978-0-12-816710-6.00001-8.
- (13) Liang, B.; He, X.; Hou, J.; Li, L.; Tang, Z. Membrane Separation in Organic Liquid: Technologies, Achievements, and Opportunities. *Adv. Mater.* **2019**, *31* (45), 1–14.
- (14) Park, H. B.; Kamcev, J.; Robeson, L. M.; Elimelech, M.; Freeman, B. D. Maximizing the Right Stuff: The Trade-off between Membrane Permeability and Selectivity. *Science (80-.)*. **2017**, *356* (6343), 1138–1148.
- (15) Low, Z.-X.; Wang, H. Challenges in Membrane-Based Liquid Phase Separations. *Green Chem. Eng.* **2021**, *2* (1), 3–13.
- (16) Li, X.; Liu, J.; Qu, R.; Zhang, W.; Liu, Y.; Zhai, H.; Wei, Y.; Hu, H.; Feng, L. Universal and Tunable Liquid-Liquid Separation by Nanoparticle-Embedded Gating Membranes Based on a Self-Defined Interfacial Parameter. *Nat. Commun.* **2021**, *12* (1), 1–10.
- (17) Merlet, R. B.; Pizzoccaro-Zilamy, M. A.; Nijmeijer, A.; Winnubst, L. Hybrid Ceramic Membranes for Organic Solvent Nanofiltration: State-of-the-Art and Challenges. *J. Membr. Sci.* **2020**, *599*, 117839.
- (18) Zou, D.; Fan, Y. State-of-the-Art Developments in Fabricating Ceramic Membranes with Low Energy Consumption. *Ceram. Int.* **2021**, *47* (11), 14966–14987.
- (19) Munirasu, S.; Haija, M. A.; Banat, F. Use of Membrane Technology for Oil Field and Refinery Produced Water Treatment - A Review. *Process Saf. Environ. Prot.* **2016**, *100*, 183–202.
- (20) Bennett, A. Fine Chemicals: Membrane Technology in the Fine Chemicals Industry. *Filtr. Sep.* **2010**, *47* (3), 16–19.
- (21) Pinnau, I.; Freeman, B. D. Formation and Modification of Polymeric Membranes: Overview. *ACS Symp. Ser.* **1999**, *744*, 1–22.
- (22) Darvishmanesh, S.; Degreè, J.; Van Der Bruggen, B. Mechanisms of Solute Rejection in Solvent Resistant Nanofiltration: The Effect of Solvent on Solute Rejection. *Phys. Chem. Chem. Phys.* **2010**, *12* (40), 13333–13342.
- (23) Zhang, Y.; Zhong, M.; Luo, B.; Li, J.; Yuan, Q.; Yang, X. J. The Performance of Integrally Skinned Polyetherimide Asymmetric Nanofiltration Membranes with Organic Solvents. *J. Membr. Sci.* **2017**, *544*, 119–125.
- (24) Shen, J.; Beale, K.; Amura, I.; Emanuelsson, E. A. C. Ligand and Solvent Selection for Enhanced Separation of Palladium Catalysts by Organic Solvent Nanofiltration. *Front. Chem.* **2020**, *8* (May), 1–10.
- (25) Volkov, A. V.; Parashchuk, V. V.; Stamatialis, D. F.; Khotimsky, V. S.; Volkov, V. V.; Wessling, M. High Permeable PTMSP/PAN Composite Membranes for Solvent Nanofiltration. *J. Membr. Sci.* **2009**, *333* (1–2), 88–93.
- (26) Werhan, H.; Farshori, A.; Rudolf von Rohr, P. Separation of Lignin Oxidation Products by Organic Solvent Nanofiltration. *J. Membr. Sci.* **2012**, *423–424*, 404–412.
- (27) Buonomenna, M. G.; Bae, J. Organic Solvent Nanofiltration in Pharmaceutical Industry. *Sep. Purif. Rev.* **2015**, *44* (2), 157–182.
- (28) Ingold, C. K.; Ingold, E. H. CLXIX. - The Nature of the Alternating Effect in Carbon Chains. Part V. A Discussion of Aromatic Substitution with Special Reference to the Respective Rôles of Polar and Non-Polar Dissociation; and a Further Study of the Relative Directive Efficiencies Of. *J. Chem. Soc.* **1926**, *129*, 1310–1328.
- (29) Ziaei-Moayyed, M.; Goodman, E.; Williams, P. Electrical Deflection of Polar Liquid Streams: A Misunderstood Demonstration. *J. Chem. Educ.* **2000**, *77* (11), 1520–1524.
- (30) Chau, J.; Basak, P.; Sirkar, K. K. Reverse Osmosis Separation of Particular Organic Solvent Mixtures by a Perfluorodioxole Copolymer Membrane. *J. Membr. Sci.* **2018**, *563* (May), 541–551.
- (31) El-Samak, A. A.; Ponnamm, D.; Hassan, M. K.; Ammar, A.; Adham, S.; Al-Maadeed, M. A. A.; Karim, A. Designing Flexible and Porous Fibrous Membranes for Oil Water Separation—A Review of Recent Developments. *Polym. Rev.* **2020**, *60* (4), 671–716.
- (32) White, L. S.; Nitsch, A. R. Solvent Recovery from Lube Oil Filtrates with a Polyimide Membrane. *J. Membr. Sci.* **2000**, *179* (1–2), 267–274.
- (33) Junaidi, N. F. D.; Othman, N. H.; Shahrudin, M. Z.; Alias, N. H.; Marpani, F.; Lau, W. J.; Ismail, A. F. Fabrication and Characterization of Graphene Oxide-Polyethersulfone (GO-PES) Composite Flat Sheet and Hollow Fiber Membranes for Oil-Water Separation. *J. Chem. Technol. Biotechnol.* **2020**, *95* (5), 1308–1320.
- (34) Park, E. J.; Kim, H. J.; Han, S. W.; Jeong, J. H.; Kim, I. H.; Seo, H. O.; Kim, Y. D. Assembly of PDMS/SiO₂-PTFE and Activated Carbon Fibre as a Liquid Water-Resistant Gas Sorbent Structure. *Chem. Eng. J.* **2017**, *325*, 433–441.
- (35) Uragami, T. *2.10 Selective Membranes for Purification and Separation of Organic Liquid Mixtures*; Elsevier Ltd., 2017; Vol. 2. DOI: 10.1016/b978-0-12-409547-2.12255-3.
- (36) Yang, Y.; Bai, P.; Guo, X. Separation of Xylene Isomers: A Review of Recent Advances in Materials. *Ind. Eng. Chem. Res.* **2017**, *56* (50), 14725–14753.
- (37) Shi, Q.; Gonçalves, J. C.; Ferreira, A. F. P.; Rodrigues, A. E. A Review of Advances in Production and Separation of Xylene Isomers. *Chem. Eng. Process. - Process Intensif.* **2021**, *169*, 108603.
- (38) Zhan, W.; Xu, Z.; Yang, X. Molecular Interlayer Intercalation of Ethanol-Water Mixture towards GO Laminated Membranes. *Sep. Purif. Technol.* **2020**, *233*, 116029.
- (39) Differences Between Glycolic Acid & Glycerin. <https://sciencing.com/differences-between-glycolic-acid-glycerin-8062972.html> (accessed 2021-06-22).
- (40) Grushevenko, E. A.; Borisov, I. L.; Knyazeva, A. A.; Volkov, V. V.; Volkov, A. V. Polyalkylmethylsiloxanes Composite Membranes for Hydrocarbon/Methane Separation: Eight Component Mixed-Gas Permeation Properties. *Sep. Purif. Technol.* **2020**, *241*, 116696.

- (41) Tang, Y.; Dubbeldam, D.; Tanase, S. Water-Ethanol and Methanol-Ethanol Separations Using in Situ Confined Polymer Chains in a Metal-Organic Framework. *ACS Appl. Mater. Interfaces* **2019**, *11* (44), 41383–41393.
- (42) See-Toh, Y. H.; Silva, M.; Livingston, A. Controlling Molecular Weight Cut-off Curves for Highly Solvent Stable Organic Solvent Nanofiltration (OSN) Membranes. *J. Membr. Sci.* **2008**, *324* (1–2), 220–232.
- (43) Soroko, I.; Lopes, M. P.; Livingston, A. The Effect of Membrane Formation Parameters on Performance of Polyimide Membranes for Organic Solvent Nanofiltration (OSN): Part A. Effect of Polymer/Solvent/Non-Solvent System Choice. *J. Membr. Sci.* **2011**, *381* (1–2), 152–162.
- (44) Young, T. H.; Chen, L. W. Pore Formation Mechanism of Membranes from Phase Inversion Process. *Desalination* **1995**, *103* (3), 233–247.
- (45) Barzin, J.; Sadatnia, B. Correlation between Macrovoid Formation and the Ternary Phase Diagram for Polyethersulfone Membranes Prepared from Two Nearly Similar Solvents. *J. Membr. Sci.* **2008**, *325* (1), 92–97.
- (46) Bieniek, A.; Terzyk, A. P.; Wisniewski, M.; Roszek, K.; Kowalczyk, P.; Sarkisov, L.; Keskin, S.; Kaneko, K. MOF Materials as Therapeutic Agents, Drug Carriers, Imaging Agents and Biosensors in Cancer Biomedicine: Recent Advances and Perspectives. *Prog. Mater. Sci.* **2021**, *117*, 100743.
- (47) Qiu, S.; Xue, M.; Zhu, G. Metal-Organic Framework Membranes: From Synthesis to Separation Application. *Chem. Soc. Rev.* **2014**, *43* (16), 6116–6140.
- (48) Chen, L.; Wang, H. F.; Li, C.; Xu, Q. Bimetallic Metal-Organic Frameworks and Their Derivatives. *Chem. Sci.* **2020**, *11* (21), 5369–5403.
- (49) Yu, S.; Pang, H.; Huang, S.; Tang, H.; Wang, S.; Qiu, M.; Chen, Z.; Yang, H.; Song, G.; Fu, D.; Hu, B.; Wang, X. Recent Advances in Metal-Organic Framework Membranes for Water Treatment: A Review. *Sci. Total Environ.* **2021**, *800*, 149662.
- (50) Morris, R. E.; Brammer, L. Coordination Change, Lability and Hemilability in Metal-Organic Frameworks. *Chem. Soc. Rev.* **2017**, *46* (17), 5444–5462.
- (51) Li, X.; Liu, Y.; Wang, J.; Gascon, J.; Li, J.; Van Der Bruggen, B. Metal-Organic Frameworks Based Membranes for Liquid Separation. *Chem. Soc. Rev.* **2017**, *46* (23), 7124–7144.
- (52) Campbell, J.; Burgal, J. D. S.; Szekeley, G.; Davies, R. P.; Braddock, D. C.; Livingston, A. Hybrid Polymer/MOF Membranes for Organic Solvent Nanofiltration (OSN): Chemical Modification and the Quest for Perfection. *J. Membr. Sci.* **2016**, *503*, 166–176.
- (53) Zhang, X.; Cheng, F. Y.; Zhang, H. Z.; Xu, Z. L.; Xue, S. M.; Ma, X. H.; Xu, X. R. In-Situ Synthetic Modified Metal-Organic Framework (MZIF-8) as an Interlayer of the Composite Membranes for Ethanol Dehydration. *J. Membr. Sci.* **2020**, *601*, 117916.
- (54) Echaide-Górriz, C.; Sorribas, S.; Téllez, C.; Coronas, J. MOF Nanoparticles of MIL-68(Al), MIL-101(Cr) and ZIF-11 for Thin Film Nanocomposite Organic Solvent Nanofiltration Membranes. *RSC Adv.* **2016**, *6* (93), 90417–90426.
- (55) Sarango, L.; Paseto, L.; Navarro, M.; Zornoza, B.; Coronas, J. Controlled Deposition of MOFs by Dip-Coating in Thin Film Nanocomposite Membranes for Organic Solvent Nanofiltration. *J. Ind. Eng. Chem.* **2018**, *59*, 8–16.
- (56) Ma, D.; Han, G.; Gao, Z. F.; Chen, S. B. Continuous UiO-66-Type Metal-Organic Framework Thin Film on Polymeric Support for Organic Solvent Nanofiltration. *ACS Appl. Mater. Interfaces* **2019**, *11*, 45290.
- (57) Namvar-Mahboub, M.; Pakizeh, M.; Davari, S. Preparation and Characterization of UZM-5/Polyamide Thin Film Nanocomposite Membrane for Dewaxing Solvent Recovery. *J. Membr. Sci.* **2014**, *459*, 22–32.
- (58) Namvar-Mahboub, M.; Pakizeh, M. Development of a Novel Thin Film Composite Membrane by Interfacial Polymerization on Polyetherimide/Modified SiO₂ Support for Organic Solvent Nanofiltration. *Sep. Purif. Technol.* **2013**, *119*, 35–45.
- (59) Li, Y.; Mao, H.; Zhang, H.; Yang, G.; Ding, R.; Wang, J. Tuning the Microstructure and Permeation Property of Thin Film Nanocomposite Membrane by Functionalized Inorganic Nanospheres for Solvent Resistant Nanofiltration. *Sep. Purif. Technol.* **2016**, *165*, 60–70.
- (60) Li, S.; Li, C.; Song, X.; Su, B.; Mandal, B.; Prasad, B.; Gao, X.; Gao, C. Graphene Quantum Dots-Doped Thin Film Nanocomposite Polyimide Membranes with Enhanced Solvent Resistance for Solvent-Resistant Nanofiltration. *ACS Appl. Mater. Interfaces* **2019**, *11*, 6527–6540.
- (61) Wang, C.; Park, M. J.; Seo, D. H.; Drioli, E.; Matsuyama, H.; Shon, H. Recent Advances in Nanomaterial-Incorporated Nanocomposite Membranes for Organic Solvent Nanofiltration. *Sep. Purif. Technol.* **2021**, *268* (March), 118657.
- (62) Li, S.; Li, C.; Su, B.; Hu, M. Z.; Gao, X.; Gao, C. Amino-Functionalized Graphene Quantum Dots (AGQDs)-Embedded Thin Film Nanocomposites for Solvent Resistant Nanofiltration (SRNF) Membranes Based on Covalence Interactions. *J. Membr. Sci.* **2019**, *588*, 117212.
- (63) Liang, Y.; Li, C.; Li, S.; Su, B.; Hu, M. Z.; Gao, X.; Gao, C. Graphene Quantum Dots (GQDs)-Polyethyleneimine as Interlayer for the Fabrication of High Performance Organic Solvent Nanofiltration (OSN) Membranes. *Chem. Eng. J.* **2020**, *380*, 122462.
- (64) Paseto, L.; Luque-Alled, J. M.; Malankowska, M.; Navarro, M.; Gorgojo, P.; Coronas, J.; Téllez, C. Functionalized Graphene-Based Polyamide Thin Film Nanocomposite Membranes for Organic Solvent Nanofiltration. *Sep. Purif. Technol.* **2020**, *247*, 116995.
- (65) Tham, H. M.; Japip, S.; Chung, T. S. WS₂ Deposition on Cross-Linked Polyacrylonitrile with Synergistic Transformation to Yield Organic Solvent Nanofiltration Membranes. *J. Membr. Sci.* **2019**, *588* (June), 117219.
- (66) Jiang, S.; Li, Y.; Ladewig, B. P. A Review of Reverse Osmosis Membrane Fouling and Control Strategies. *Sci. Total Environ.* **2017**, *595*, S67–S83.
- (67) Teng, Z.; Wang, B.; Hu, Y.; Zhang, W.; Wu, Z.; Xu, D. High Performance Ultrafiltration Membrane by Coupling Magnetic Migration and In-Situ Surface Modification. *Polym. Test.* **2021**, *101*, 107306.
- (68) Choudhury, R. R.; Gohil, J. M.; Mohanty, S.; Nayak, S. K. Antifouling, Fouling Release and Antimicrobial Materials for Surface Modification of Reverse Osmosis and Nanofiltration Membranes. *J. Mater. Chem. A* **2018**, *6* (2), 313–333.
- (69) Saqib, J.; Aljundi, I. H. Membrane Fouling and Modification Using Surface Treatment and Layer-by-Layer Assembly of Polyelectrolytes: State-of-the-Art Review. *J. Water Process Eng.* **2016**, *11*, 68–87.
- (70) Joo, M.; Shin, J.; Kim, J.; You, J. B.; Yoo, Y.; Kwak, M. J.; Oh, M. S.; Im, S. G. One-Step Synthesis of Cross-Linked Ionic Polymer Thin Films in Vapor Phase and Its Application to an Oil/Water Separation Membrane. *J. Am. Chem. Soc.* **2017**, *139* (6), 2329–2337.
- (71) Gao, K.; Kearney, L. T.; Wang, R.; Howarter, J. A. Enhanced Wettability and Transport Control of Ultrafiltration and Reverse Osmosis Membranes with Grafted Polyelectrolytes. *ACS Appl. Mater. Interfaces* **2015**, *7* (44), 24839–24847.
- (72) Amirilargani, M.; Sadrzadeh, M.; Sudhölter, E. J. R.; de Smet, L. C. P. M. Surface Modification Methods of Organic Solvent Nanofiltration Membranes. *Chem. Eng. J.* **2016**, *289*, 562–582.
- (73) Ayyavoo, J.; Nguyen, T. P. N.; Jun, B. M.; Kim, I. C.; Kwon, Y. N. Protection of Polymeric Membranes with Antifouling Surfacing via Surface Modifications. *Colloids Surfaces A Physicochem. Eng. Asp.* **2016**, *506*, 190–201.