Toward the Next Generation of Sustainable Membranes from Green Chemistry Principles

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ABSTRACT: Large-scale membrane technology has been widely implemented and rapidly growing for roughly 40 years. However, considering its entire life cycle, there are aspects characterized by low sustainability, and this industry certainly cannot be defined as green. In the membrane manufacturing process, raw materials mainly rely on non-biodegradable petroleum-based polymers and hazardous solvents. These materials are thus connected to the energy crisis and are associated to burdens relatd to their disposal, while also osing risks to workers and the environment. Therefore, bio-based polymers and green solvents should be employed in the membrane preparation process and replace traditional ones. Moreover, the wastewater generated from membrane fabrication processes contains organic solvents and should be efficiently treated or recycled before discharge. Finally, a large number of spent membrane elements should also be reused and recovered, rather than landfilled. This review critically evaluates the recent advances in methods to improve the sustainability of membrane technology, specifically emphasizing the progresses made around the above aspects, and analyzes the needs for membrane industry transformations in the light of circular economy.

INTRODUCTION

Membrane technology has been increasingly applied in diverse industrial processes, for example, in water treatment and gas separation, in the chemical and pharmaceutical industry, in the food and beverage industry, for hemodialysis, or textile processing. [1-3] In the water treatment field, membrane technology plays a key role to promote safe potable water supply, wastewater reuse, desalination, and environmental protection. [4-6] Hydrogen recovery, nitrogen enrichment, oxygen separation, carbon dioxide capture, and natural gas purification, can be realized efficiently by gas separation membranes. [7, 8] In addition, membrane technology has also been applied in metallurgy, energy, electronics, and progressively more novel fields. [1]

Membrane technology has several key advantages over traditional technologies. [9] Membrane-based separation is characterized by sharp selectivity, while being associated with simple equipment and conveniently compact structures. [10] It is also highly adaptable and flexible in terms of installation and operation. Furthermore, low energy consumption, low pollution, and little use of chemicals in membrane separation processes reduce the total CO_2 emission and environmental effects compared to traditional technologies. [8, 9, 11, 12] Although advantages of membrane technology are apparent, drawbacks are gradually exposed in large-scale production and deployment. For instance, petroleum-based non-biodegradable polymers are the typical materials used for membrane fabrication. And large amounts of toxic organic solvents are involved in the membrane manufacturing process, posing a series of health and environmental risks. In another typical example, hollow fibers modules are difficult to repair if broken, and this feature shortens their average life-time. In the light of the increasingly severe energy crisis and environmental

pollution problems, improving the sustainability of membrane technology and promoting the green transformation of this engineering field is imperative.

In Figure. 1a, promising strategies focusing on cradle-to-grave considerations are summarized, considering membrane manufacturing, use, and end-of-life management. These approaches are guided by the Twelve Principles of Green Chemistry, which are shown in Figure. 1b. [13, 14] We believe that gradual improvements of already existing manufacturing platforms are likely to be implemented in the foreseeable future.

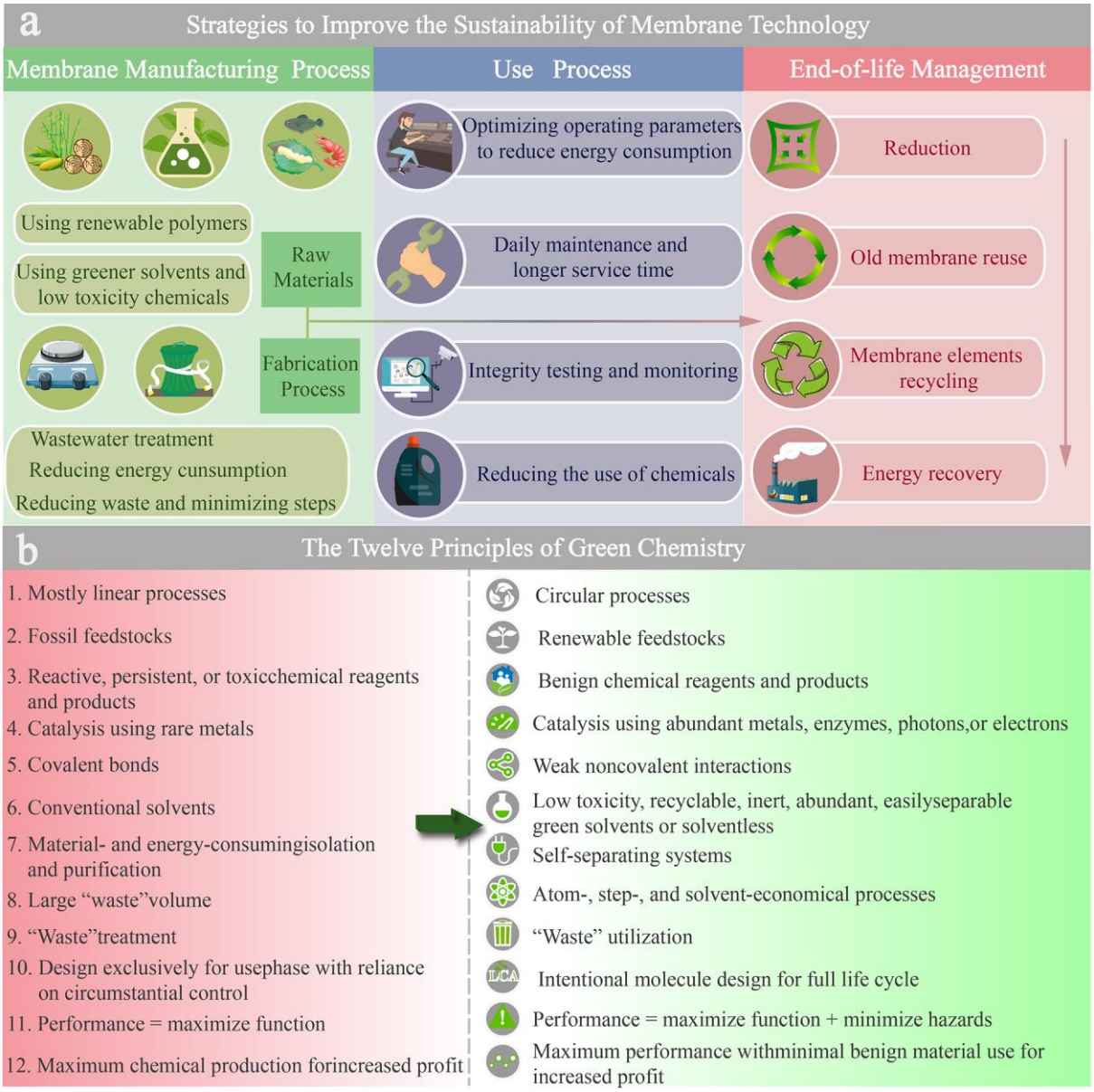

Figure. 1 Sustainable membrane industry transformation strategies from manufacturing to end-of-life management. (a) Strategies to improve the sustainability of membrane technology. (b) The Twelve Principles of Green Chemistry.

We propose five ways to improve the sustainability of the membrane manufacturing process. The first is using polymers from renewable sources (also called bio-based polymers) to partly or

entirely substitute non-biodegradable petroleum-based ones. Bio-based polymers may be used as membrane materials, nonwoven membrane supports, or additives. Nowadays, the typical polymers employed for membrane manufacturing are: poly(vinylidene fluoride) (PVDF), polyethersulfone (PESU), polysulfone (PSU), poly(ethylene terephthalate) (PET), and poly(ethylene glycol) (PEG) (Figure. 2a). These materials are non-renewable and difficult to degrade: both their production and disposal are not sustainable. Partial substitution may be a relatively easy first step in the efforts to completely substitute these materials. [15-17] However, it is worth noting that not all bio-based polymers are biodegradable. Some non-biodegradable bio-based polymers, such as bioderived PET, can be applied to fabricate membranes for wastewater treatment, whereby biodegradable membranes are not always suitable. Polymers can also be recycled or reused in circular economy. [18]

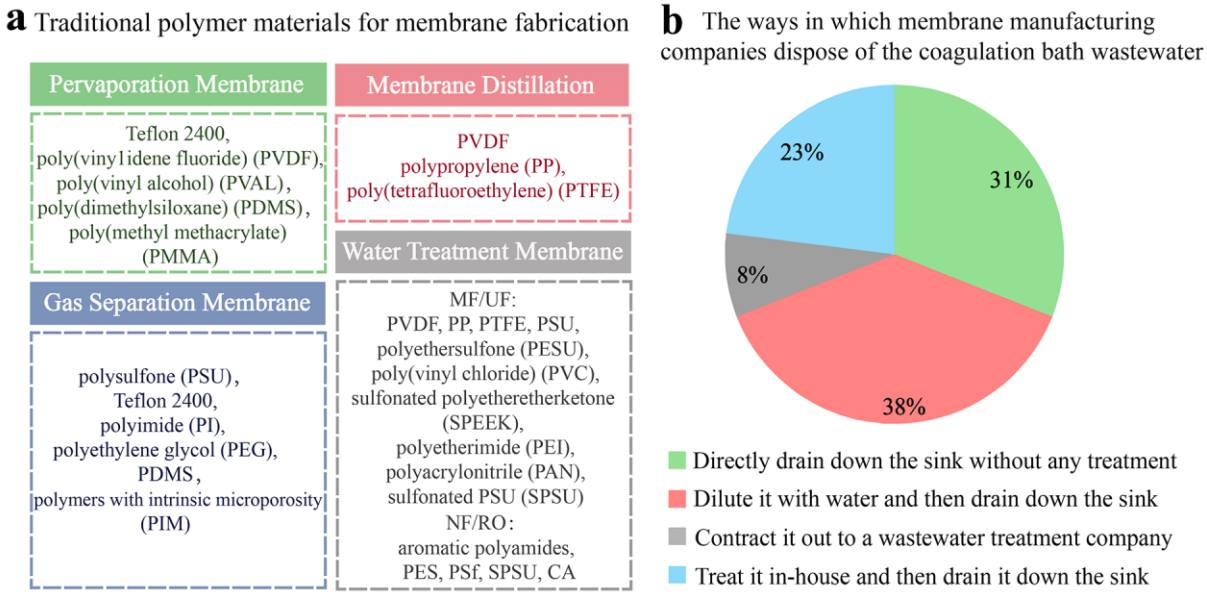

Figure 2. (a) Traditional polymer materials for membrane fabrication. (b) The main outcome of a survey from Razali *et al.* regarding the way in which membrane manufacturing companies dispose of the wastewater from the phase inversion coagulation bath. [19]

Furthermore, greener solvents should be used to substitute traditional ones. Traditional solvents typically used for membrane fabrication, such as N, N-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP), and dimethylformamide (DMF), are harmful to the environment, and pose risks to the health and safety of membrane manufacturing workers. [13, 20, 21] Their detailed dangers are listed in Table S1 (Supporting Information, SI), and the European REACH Regulation identifies them as substances of very high concern (SVHC). [22] In the last decade, there have been some advances around the use of green solvents for membrane fabrication, and a series of nontoxic, biodegradable, and recyclable green solvents (*e.g.*, PolarClean and Cyrene) have been applied and shown to provide comparable or even superior performance compared with traditional solvents. [9, 23-26]

Thirdly, the wastewater (mainly containing organic solvents and polymers) generated from membrane fabrication should be treated and recycled. It is estimated that membrane production generates over 50 billion liters of wastewater annually worldwide, contributing to more than 95% of the total waste generated during the membrane fabrication process. [19, 27] However, only 31% of this waste is being somehow treated nowadays, [19] as presented in Figure 2b. The fourth strategy in the manufacturing process is reducing the number of steps for membrane fabrication, which would translate into a reduction of toxic waste, energy consumption, and costs. From this point of view, tuning of the membranes via blending is a best option rather than post-fabrication surface grafting, while surface physical coating is to be preferred over elaborate chemical functionalizations involvoing several pre- and post-modification steps. Finally, the membrane casting solutions should be dissolved at room temperature to reduce energy consumption.

In the membrane operational phase, we propose four strategies to improve sustainability. First, measures to reduce the energy consumption should be taken into consideration, including

optimizing the transmembrane pressure, membrane modules structure, physical backwashing time, and other operating parameters. Artificial intelligence and related in silico fields may provide further help improving the efficiency of the membrane fabrication process. Second, daily maintenance is of vital importance to extend the service time of membrane modules. Third, integrity testing and continuous monitoring are useful to ensure the stable and efficient operation of membrane modules, and guarantee the suitable quality of the permeate. The direct integrity testing is a physical process that is sufficiently sensitive to detect a 3-μm breach in membrane modules, and it should be conducted at least once per day. The continuous indirect integrity monitoring is the measurement of the product stream quality parameter, and should be performed at least every 15 min. The membrane fibers, fabricated by high-molecular-weight polymers, are difficult to repair once they are fractured. In order to prolong their lifetime and improve sustainability, readily repairable polymer materials or self-healing materials for membrane fabrication are of interest for many researchers and engineers. [28, 29] Fourth, in the chemical cleaning process, the chemicals should be as few as possible.

The end-of-life management of spent membrane modules is also an important aspect given that large numbers of membrane elements are discarded annually. Considering reverse osmosis (RO) alone, over 14,000 tons of RO modules are discharged annually worldwide, while this number is even higher for ultrafiltration (UF) and microfiltration (MF) membranes. [1, 30] All these numbers are continuously increasing. Typical methods to dispose of these spent membrane elements are landfill or incineration, neither of which is satisfactory from a sustainability viewpoint. When landfill disposal is chosen, one must consider that the current petroleum-based elements do not degrade biologogically and will persist in the environment, threatening the soil and underground

water. As for incineration, this process produces air pollution and greenhouse gases. The correct end-of-life management methods should encompass reuse, recycling and recovery (Figure 3b).

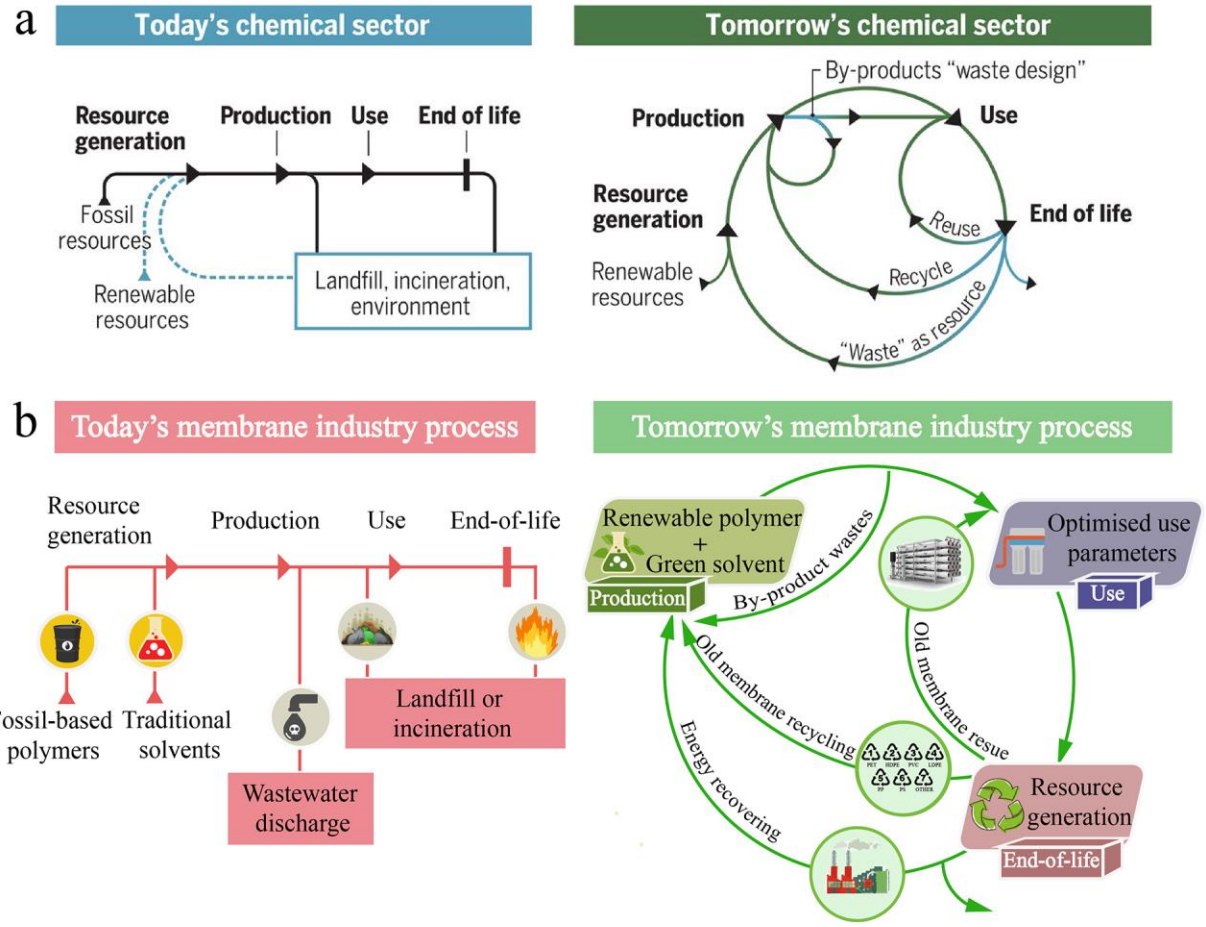

Figure 3. (a) From linear processes to circular processes in the chemical sector. [14] (b) Membrane industry transformation: from linear process to circular process.

This review covers the following cutting-edge aspects required to improve the sustainability of membrane technology: i) bio-based polymers for membrane manufacturing, ii) green solvents for membrane manufacturing, iii) treatment and recycling of the wastewater from membrane manufacturing, iv) the application of artificial intelligence in membrane technology and v) end-of-life management of spent membrane modules. We believe that lower toxicity, lower environmental persistence, smart platforms, and circular economy are key factors of the next-

generation membrane technology. [31] This review introduces recent advances around these aspects to provide some inspiration for membrane scientists and enterprise manufacturers, guiding and promoting the sustainable transformation of the entire industry.

BIO-BASED POLYMERS FOR MEMBRANE MANUFACTURING

In the last decades, petroleum-based polymers have dominated the membrane market. There is no doubt that these polymers are economical, versatile, as well as thermally and chemically stable, [32] but their negative impacts on the environment is not negligible. The exploitation, transportation, and refining processes of crude oil may cause marine pollution and air pollution, as well as an increase in the carbon footprint. Also, petroleum is non-renewable and is depleting worldwide. [33]

To cope with these problems, we should incorporate bio-based polymers into the membrane preparation process. Some bio-based polymers are found naturally, such as cellulose and chitosan, while biosynthetic routes may be pursued to obtain many others. These materials usually exhibit high hydrophilicity, biocompatibility, and biodegradability, as well as low toxicity, carbon footprint, and environmental impact. Bacterial fermentation, vegetables, and animals are the dominant resources of bio-based polymers, as depicted in Figure 4.

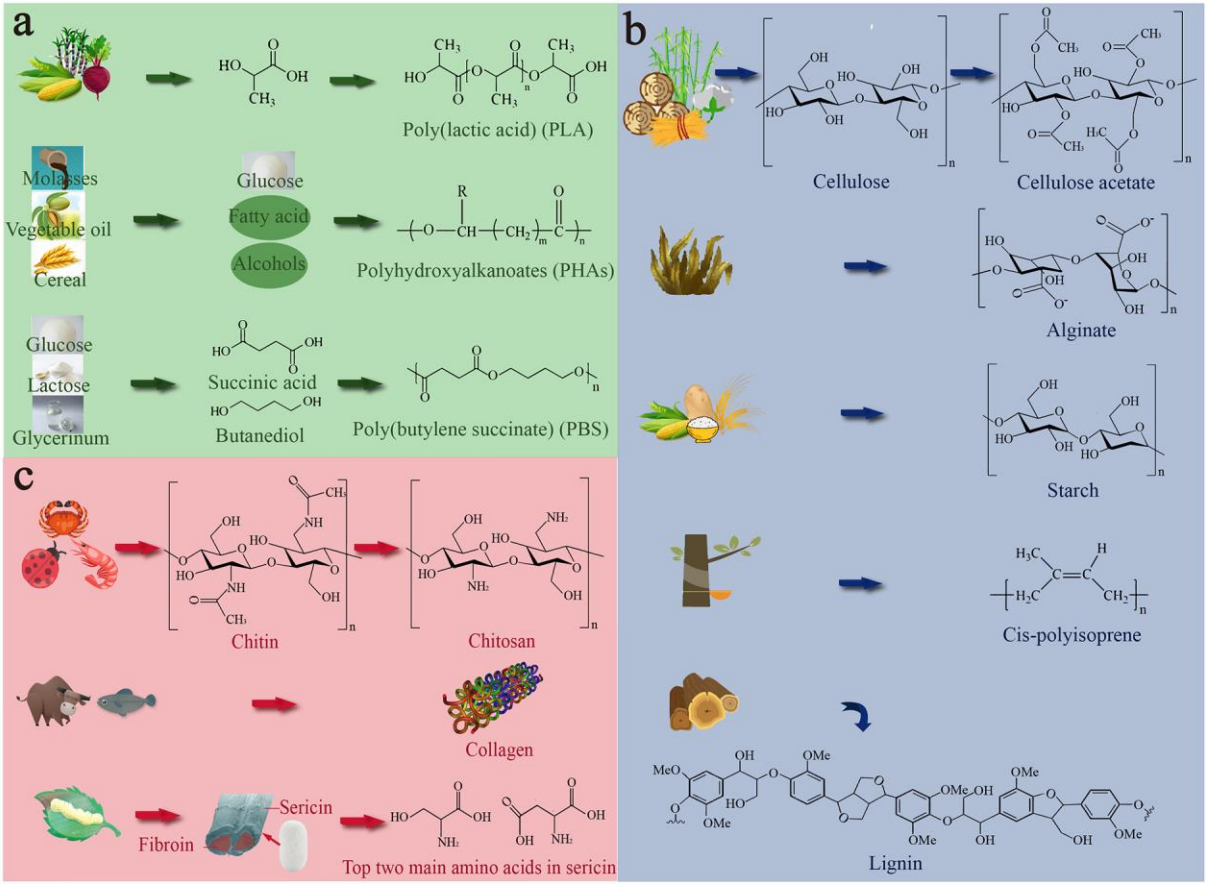

Figure 4. The structural formula of typical bio-based polymers derived from (a) bacterial fermentation products, (b) vegetable sources, and (c) animal sources.

Bio-based Polymers from Bacterial Fermentation

Poly(lactic acid) (PLA). PLA is an environmentally benign aliphatic polyester. It derives from the activity of lactic acid bacteria using agricultural products and by-products as initial substrate, such as corn, sugarcane, and sugar beets; it is biodegraded naturally by hydrolysis, generating H_2O, CO_2, and humus. [34] PLA has suitable mechanical and physical properties, which can be compared to those of many petroleum-based polymers. The price of PLA was very high before the late 1980s; [35] however, a patented, low-cost continuous production process was developed by Cargill Dow LLC, decreasing the price and promoting commercial production and promotion of PLA. [34] Today,

the applications of PLA have expanded to packaging, the medical and the automotive industries, textiles, films, personal hygiene products, and 3D printing, [34, 36-38] showing a bright future.

Thanks to its good biocompatibility, PLA in membrane fabrication was first applied in health and medical sciences, as a scaffold for human cell growth and as a support for the controlled release of medicines. [39-41] In addition, PLA can be effectively used alone or blended with other polymers to fabricate MF and UF membranes via various methods: non-solvent induced phase separation (NIPS), [42] thermally induced phase separation (TIPS), [35, 43] vapor-induced phase separation (VIPS), [38, 44-46] and electrospinning. [41, 47] In the future, 3D or 4D printed membrane may be produced with PLA, which is a promising green method for membrane manufacturing. In composite membranes, support layers can be fabricated by the same routes. For example, Le Phuong et al. [27] fabricated sustainable, biodegradable, nonwoven composite membrane supports from PLA and bamboo fiber (consisting of cellulose, lignin, and hemicellulose), which provided a sustainable alternative for conventional membrane backing materials. A schematic of the fabrication procedure is shown in Figure S1 (SI).

Polyhydroxyalkanoates (PHAs). PHAs can be produced from renewable resources, such as lipids, carbohydrates, alcohols, and organic acids. [48] They are environmentally friendly bio-based polymers with suitable biocompatibility and biodegradability. [48-50] Therefore, their main application is in the biomedical field. [51-53] More than 150 kinds of different monomer structures of PHAs have been reported. [54] However, only a few have been commercialized: poly(3-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and poly(3-hydroxybutyrateco-3-hydroxyhexanoate) (PHBHHx). [55]

There has been little research on PHAs for membrane fabrication. It is worth noting that PHAs are totally insoluble in water and most organic solvents, except some halogenated solvents, such

as chloroform. [32] Therefore, PHB, PHBV, and PHBHHx membranes can be produced by VIPS with chloroform as the solvent. [49, 51] However, given that chloroform is toxic, this specific system is not sustainable. Whether there is a possibility of PHAs application in membrane engineering and in other fields is a question worth exploring.

Poly(butylene succinate) (PBS). PBS is one of the most promising biodegradable aliphatic polyesters with suitable biocompatibility, biodegradability, excellent processability, as well as thermal and chemical resistance. [56, 57] It can be obtained by polymerization of butanediol and succinic acid, both of which are from bio-based renewable resources. The cost of PBS is relatively low compared to many other biopolymers. [58]

There has been some research around the use of PBS to fabricate membranes. Jeong et al. [56] prepared the first PBS membranes by electrospinning, obtaining uniform nanoporous threads by dissolving PBS in chloroform. [59] However, it was found that the membranes were soft and had low separation performance. [60] Therefore, gelatin, a natural protein, was used to blend with PBS or as a coating layer to improve its mechanical properties. [57, 61] Overall, PBS membranes have been limited due to the poor mechanical properties. To overcome this issue, PBS may be blended with PLA, [62-64] PESU, [65] or cellulose acetate (CA) [66, 67]: the resulted membranes have shown improved mechanical characteristics.

Bio-based Polymers from Vegetable Sources

Cellulose and Its Derivatives. Cellulose, the most abundant polymer on earth, is a linear polysaccharide primarily derived from plant fiber, for example, wood, cotton, bamboo, straw, reeds, hemp, mulberry bark, and bagasse. In addition, it can also be generated by bacteria (*e.g.*, *Acetobacter xylinum* or *Acanthamoeba castellani*) and algae (*e.g.*, Valonia ventricosa). [68, 69] Cellulose exhibits suitable hydrophilicity and biocompatibility, excellent mechanical strength (the

ultimate tensile strength of cellulose is estimated to be 17.8 GPa, seven times higher than that of steel), [70] and easy chemical modification with low production cost. However, its high crystallinity and strong intermolecular hydrogen bonds reduce the solubility in common solvents, limiting the membrane fabrication. [71] The solvents that have been used to obtain cellulose-based membranes are listed in Table 1.

Table 1. Solvents Used for Cellulose Membrane Manufacturing

Solvents	Classification	Features	Ref.
NMMO[a]	Organic solvent	Commercially used	72
Hydrazine/LiSCN, NaSCN, or KSCN	Hydrazine/thiocyanate salt	Toxic	73
DMAc/LiCl	Organic solvents with dissolved salts	Toxic	70
NMP/LiCl			74
NaOH/ urea/ DI water (7:12:81 by wt.%)	Alkali	Low cost and low toxicity	75
$LiOH{\cdot}H_2O$/urea/DI water (8:15:77 by wt. %)			71
AMIMCl[b]			76
[EMIM] [OAc][c]	Ionic liquid	Low toxicity, expensive, and difficult to commercialize	77, 78
[DMIM][DMP][d]			79
[EMIM] [DEP][e]			79
[C_4mim] [Cl][f]			80

Note: NMMO[a]: N-methylmorpholine-N-oxide

AMIMCl[b]: 1-allyl-3-methylimidazolium chloride

[EMIM] [OAc][c]: 1-ethyl-3-methyl imidazolium acetate

[DMIM][DMP][d]: 1,3-dimethylimidazolium dimethyl phosphate

[EMIM] [DEP][e]: 1-ethyl-3-methyimidazolium diethyl phosphate

[C_4mim] [Cl][f]: 1butyl-3-methylimidazolium chloride

Creatively, Eggensperger et al. [28] utilized the symbiotic culture of yeast and bacteria with kombucha tea, and the cellulose fibers they produced can form a living water filtration membrane (Figure S2, SI). The surface of the membrane can heal after a puncture or incision. This interesting self-healing living membrane avoided petroleum-based polymers and harmful solvents, and the low-tech process may potentially bring accessible water treatment to anyone and anywhere.

Cellulose derivatives have been developed to overcome some cellulose limitations. Such derivatives are the products of esterification or etherification of hydroxyl in cellulose macromolecules, [69] and some have been used as membrane materials, such as cellulose acetate (CA), cellulose acetate butyrate (CAB), [81] hydroxyethyl cellulose (HEC), [82] cellulose triacetate (CTA), [83] and ethyl cellulose (EC). [84] CA, the most common and promising cellulose derivative, can be produced by treating cellulose with acetic acid, acetic anhydride, and sulphuric acid as a catalyst. [85] It can be dissolved in many common organic solvents, such as acetic acid, acetone, DMAc, DMF. Also, it has a tunable polymeric network with pore sizes customizable over a wide range for MF, UF, NF, RO, and FO membrane fabrication. [86-88] Abundant research has encompassed the fabrication of CA membranes for oil/water separation, [89, 90] desalination, [91] and wastewater treatment. [92, 93] Important drawbacks of CA membranes are that they function well in a narrow pH range of 3-8 and have limited lifespan. Cellulose derived bio-based nanomaterials, namely nanocellulose, including nanofibrillated cellulose (NFC), cellulose nanocrystal (CNC) and bacterial nanocellulose (BNC), are also emerging green materials for membrane fabrication. [94, 95]

Their inherently high crystallinity and hydrogen-bonding propensity promote the formation of films with excellent gas-barrier properties. [95]

Lignin. Lignin is the second most abundant polymer on earth after cellulose, serving as structural support to cell walls. [96] It can be biodegraded by some microorganisms, such as white-rot fungi. Lignin has high potential, being the only renewable aromatics feedstock. [97, 98] However, it is also among the most challenging bio-based polymers because of its complexity. Currently, commercial lignin-based polymeric products are almost negligible in volume.

In the membrane manufacturing process, lignin has been blended with other polymers, such as poly(vinyl alcohol) (PVAL) [99] and polyacrylonitrile (PAN), [100] to compensate for the poor mechanical properties of lignin fibers. Moreover, it has also been used as a component of non-woven membrane supports. [27] Lignin is a promising membrane or non-woven support material, but the research is limited due to its complexity in extraction, purification, effective blending, and defragmentation. [18] The current utilization of lignin is in two major approaches, both of which suffer from challenges: lignin as a whole, or defragmentation of lignin into monomers and then polymers. Using lignin as a whole may lead to poor performance, while defragmentation is too costly. [18, 101] More efforts from chemistry, materials, and processing should be made to transform lignin into available materials.

Alginate. Alginate is a natural polysaccharide extracted from brown algae. It can combine with Na^+ or Ca^{2+} and produce sodium alginate (NaAlg) or calcium alginate (CaAlg). Alginate is non-toxic and has suitable biocompatibility, [102] with potential applications in the biomedical field for cell growth, drug delivery, and tissue engineering. [103]

Alginate has been increasingly employed in membrane fabrication processes in the last two decades. Its unique structure promotes the absorption of water, dyes, and heavy metals. [104]

Alginate-based materials can be applied in pervaporation dehydration, water treatment, oil-water separation, and organic solvent nanofiltration. Alginate membranes in pervaporation dehydration have outstanding separation characteristics, exceeding PVAL, ion-exchange resins, and other polysaccharides, such as chitosan and cellulose. [105] In water treatment applications, alginate membranes can adsorb trace heavy metals and dyes. [102] Alginate membranes are also ideal candidates for oil-water separation owing to their superhydrophilic and underwater superoleophobic properties. [106] However, it should be noted that alginate intrinsic water-soluble properties are associated with the presence of carboxyl and hydroxyl groups, which also lead to chemical instability in aqueous conditions. [107] Therefore, it may a good idea to blend polyanionic alginate with polycationic chitosan or to cross-link it with polyvalent metal cations (*e.g.*, Ca^{2+}), forming a stable and insoluble polyelectrolyte complex or strong gel in water. [107, 108] The alginate layer treated by calcium ions also demonstrated good stability for organic solvent nanofiltration. [109]

Starch. Starch, containing about 30% amylase, 70% amylopectin, and less than 1% lipids and proteins from plants, is an abundant natural polymer with high biodegradability and low cost. It has been widely used in the food industry to provide functional properties. [110] However, when used for membrane fabrication, starch has some intrinsic shortcomings. First, it is very hydrophilic, leading to low stability under different environmental conditions. Second, its mechanical strength and elongation behavior are poor. In order to overcome these problems, starch may be blended with other polymers, such as chitosan, CA, and PVAL. Plasticizers may also be incorporated, including glycerol and sorbitol. [32, 110-112]

Polyisoprene. Polyisoprene is produced from the trees Hevea brasiliensis (cis-polyisoprene) or Pallaquium gutta (trans-polyisoprene). [32] In addition, it can also be obtained from petroleum

refining, but synthetic polyisoprene has inferior performance than natural polyisoprene in strength and processability. Polyisoprene has wide applications in producing tires, shoes and boots, machinery, medicines, sports equipment, and latex.

The reports on fabricating polyisoprene membranes have been very few and focused on self-assembly. Mulvenna et al. [113] synthesized polyisoprene-b-polystyrene-b-poly(N,N-dimethylacrylamide) (polyisoprene–PS–PDMA) triblock polymers. Then, this polymer was used to prepare membranes by NIPS and self-assembly. This membrane may be used in water treatment, pharmaceutical separations, sensors, and drug delivery. Zhang et al. [114] fabricated polyisoprene–PS–PDMA hollow fiber membranes, exhibiting high flux and high selectivity in nanofiltration. Additionally, polyisoprene-b-polystyrene-b-poly-4-vinyl pyridine membranes [115] and polystyrene-b-polyisoprene-b-polystyrene (SIS) membranes [116] were fabricated, showing tunable structures.

Bio-based Polymers from Animal Sources

Chitosan (CS). CS is obtained from chitin via deacetylation. The amino group in the CS molecule is more active than the acetyl amino group in the chitin molecule, imparting CS with excellent biological function and chemical modification potential. [117] When the deacetylation of chitin reaches 60% degree, it becomes CS, [118] but only with the degree of more than ~70%, this material can be used as a valuable industrial product. Chitin exists in the outer shells of crustaceans, the cell membranes of fungi and algae, the shells and bones of mollusks, and the cell walls of higher plants, hence it is widely distributed in nature. CS is non-toxic, biodegradable, has suitable biocompatibility and low cost. It can be used as a membrane material for biomedical applications, pervaporation, water treatment, gas separation, as well as proton exchange of fuel cells, supercapacitors, and solid-state batteries. [119]

CS-based membranes in water treatment have been mainly applied with two objectives: (i) adsorptive membranes for phase transfer of contaminants from the aqueous solution, and (ii) composite NF/RO/FO membranes for surface separation with high solute rejection. CS-based membranes have interesting ability to adsorb contaminants, especially heavy metals, because the amino and hydroxyl groups of CS can serve as coordination sites. [120, 121] The main application of CS membranes in pervaporation has been to dehydrate aqueous-organic mixtures, and CS is arguably the most studied biodegradable material for pervaporation membranes.

However, pure CS membranes will suffer from excessive swelling and poor mechanical resistance in aqueous solutions, both phenomena impairing their performance. Therefore, avoiding CS as the bulk membrane material and using it only as the skin layer of composite membranes may be the best option. A CS skin layer can be reinforced by cross-linkers, such as glutaraldehyde, glyoxal, formaldehyde, epichlorohydrin, and isocyanates, to suppress excessive swelling, while a proper support layer can improve the overall mechanical property of composite membranes. [122]

The amino groups of CS also make this polymer a promising membrane material for CO_2 gas separation, because these moieties act as fixed carriers to facilitate the transport of acidic gases through membranes. However, it was found that the gas permeability of dry CS membranes is very low due to their dense structure. Some studies induced swelling of CS membranes with water vapor to cope with this problem, and the swollen membranes exhibited higher CO_2 gas permeabilities and selectivities. [15-17]

Collagen. Collagen exists in animal connective tissues in the skin, tendons, cartilage, and bones. In fact, animal production processes produce large amounts of collagen-rich solid waste. The recycling of this waste will also prevent the spread of harmful pathogens in the environment. [123] Collagen-based membranes are widely studied in tissue engineering due to low immune response,

which can be used as a substrate or scaffold for cell attachment, proliferation, and differentiation.[124-126]

Other collagen-based membrane applications include pervaporation [127, 128] and oil/water separation, [123, 129] but studies have been limited because collagen-based membranes biodegrade rapidly, and are sensitive to extreme pH and high temperature conditions. Moreover, collagen generally fails to achieve desired mechanical characteristics, being unable to retain its structural integrity and owing to swelling in aqueous environments. [130]

Sericin. Silk fiber is a natural polymer produced by Lepidopteron insects of the family Bombycidae and Saturniidae, and it is composed of a fibrous core protein fibroin with sericin protein surrounding it. [131] In the textile industry, sericin is the waste of degumming processes. However, it has some other applications in skin care, food, tumour suppression and wound healing, or as antioxidant, anti-apoptotic, and anticoagulant. [132-134]

As for membrane fabrication, sericin is hydrophilic and water-soluble. Pure membranes are easily swollen, thus associated with weak mechanical properties. [32] However, the structure of sericin consists of polar side chains rich in hydroxyl, carboxyl, and amino groups that enable easy cross-linking, copolymerization, or blending with other polymers to prepare membranes with high performance. [131] Sericin membranes may be applied in the biomedical field or for CO_2 separation, because the serine and glycine amino acids in its polypeptide chain can facilitate CO_2 transport. Prasad et al. [135] fabricated a CS/sericin/Na_2CO_3 active layer on a PESU support for CO_2/N_2 separation.

Dopamine (DA) and Other Biophenols. Recently, dopamine-based bioinspired coatings have been widely used for membrane surface modification.[136-139] They is utilized to achieve the superior bioadhesion properties of marine mussel byssus. [140] Via self-polymerization in an aerobic, alkaline

environment, polydopamine (PDA) layer can be formed, with high binding strength to almost all substrates, including hydrophobic membrane surfaces. PDA layers are characterized by long-time stability, easy of production, high hydrophilicity, antifouling and antibacterial properties.

For example, Wang et al. [136] reported a simultaneous polymerization of dopamine and hydrolysis of commercial tetraethoxysilane in a facile single-step process on PVDF substrates, dramatically enhancing the hydrophilicity and oil-in-water emulsion separation ability of the membrane. These authors also proved that other molecules dissolved with DA can be immobilized onto the substate during the PDA polymerization process. Other biophenols, including tannic acid, vanillyl alcohol, eugenol, morin, and quercetin, were investigated as membrane surface coatings, showing suitable performance in organic solvent nanofiltration. [138]

Recycled Materials for Membrane Manufacturing

Although most recycled materials do not belong to the category of bio-polymers, and would thus persist in the environment, their utilization for membrane fabrication is also one of the way forward, especially in instances when biodegradable membranes cannot be employed (*e.g.,* wastewater treatment). Recycled PET can be obtained from commercial water bottles, and it has in fact been used as feedstock for membrane fabrication. [141, 142] Polystyrene (PS) from plastic cups was also blended with CA to fabricate MF or UF membranes. [143]

Challenges and Outlook

In summary, bio-based polymers may be used as membrane materials or nonwoven membrane supports, showing a bright future. Bio-based membranes have been widely investigated for application in the medical field. Their biocompatibility, biodegradability, and non-toxicity are ideal characteristics for drug delivery, hemodialysis, blood oxygenation, and tissue engineering.

Moreover, bio-based membranes can also be applied in water treatment, oil-water separation, pervaporation, organic solvent nanofiltration, and gas separation, but there are some typical drawbacks: i) bio-based membranes usually have inferior mechanical properties (see in Table 2) and poor performance in harsh chemical environments; ii) the membranes can be biodegraded, thus their long-time durability is often impaired, especially in wastewater treatment applications and organic solvent nanofiltration; iii) some biopolymers used as membrane material partially or completely dissolve in water, thus the related membranes will swell in aqueous environments; iv) the hydrophobic membranes for membrane distillation, membrane crystallizers, membrane contactors *etc.* can hardly be prepared by bio-based polymers; v) the production of bio-based polymers is still small and the price of these materials is high, reducing their economic interest over petroleum-based materials (see in Table 2).

To overcome these problems, adding additives (*e.g.*, natural plasticizers, nanoparticles), cross-linking with cross-linking agents, blending with other polymers, or fabricating composite membranes whereby the biopolymer is used only in one of the different layers, are all feasible options to increase the membrane performance. Phuong et al. [144] reported that 23% of the papers dealing with organic solvent nanofiltration membranes used renewable or biodegradable materials, demonstrating solvent-resistant properties. However, the robustness of these materials has yet to be fully demonstrated. There is no doubt that further research is needed to obtain bio-based membranes having comparable or even superior performance with respect to petroleum-based membranes. Hybrid membranes consisting of petro- and bio-based polymers together, or bio-based non-biodegradable polymers, or polymers from recycled materials may represent a first step with commercial success. Another critical factor is cost, which requires carrying out technological innovation in production, constantly reducing the cost and expanding output. [145]

Table 2. Properties of Some Bio-based Polymers and Petroleum-based Polymers. The Presented Values are Collected from Other Studies. [146, 147]

Polymer	Density (g/cm^3)	Melting point (°C)	Tensile strength (MPa)	Young modulus (GPa)	Price (USD/Kg)
PLA	1.21-1.25	150-162	40-60	3-4	3-5
PHB	1.18-1.26	168-182	24-40	3.5-4	4
PHBV	1.23-1.25	144-172	20-25	0.5-1.5	3.5
PBS	1.26	114	34	0.441	NA
CA	1.3	230-300	NA	NA	10-100
Lignin	NA	NA	NA	NA	< 0.5
Sodium Alginate	NA	NA	NA	NA	12-35
Starch	1-1.39	110-115	5-6	0.125-0.85	2-5.5
CS	1	102.5	NA	NA	20-40
PP	0.9-1.16	161-170	30-40	1.1-1.6	1.1-1.5
PVDF	1.75-1.79	160-175	30-70	1.8-2.5	19-32
PESU	1.37-1.51	365-388	85-125	2.7	9-26
PSU	1.24-1.34	315-371	70-107	2.5-8.5	19-30
PVC	1.38	185-205	41-52	2.9-3.4	0.6-1.5
PAN	1.184	317	NA	NA	4-4.25

GREEN SOLVENTS FOR MEMBRANE MANUFACTURING

The current membrane fabrication process relies heavily on traditional solvents chloroform, DMF, NMP, and DMAc, posing risks to the environment and human health. Using green solvents

to substitute traditional ones is the inevitable trend in the future in both NIPS and TIPS processes. In NIPS, one of the prerequisites is that the polymer must dissolve in the solvent. The affinity between solvent and polymer also influences the phase separation pathway and the performance of the resulting membranes; therefore, selecting a proper green solvent with suitable affinity with the polymer is critical. Such affinity can be described by the R_a value, which is calculated by the Hansen solubility parameters (HSP) using the following equation: [148]

$$R_a = \sqrt{4\left(\delta_{d1}-\delta_{d2}\right)^2 + \left(\delta_{p1}-\delta_{p2}\right)^2 + \left(\delta_{h1}-\delta_{h2}\right)^2} \quad (1)$$

where δ_d, δ_p, and δ_h are the dispersion parameter (δ_d), the polar parameter (δ_p), and the hydrogen bonding parameter (δ_h). [148] A small R_a value indicates high polymer-solvent compatibility, and the polymer will most probably be soluble in that solvent, as shown in Figure 5.

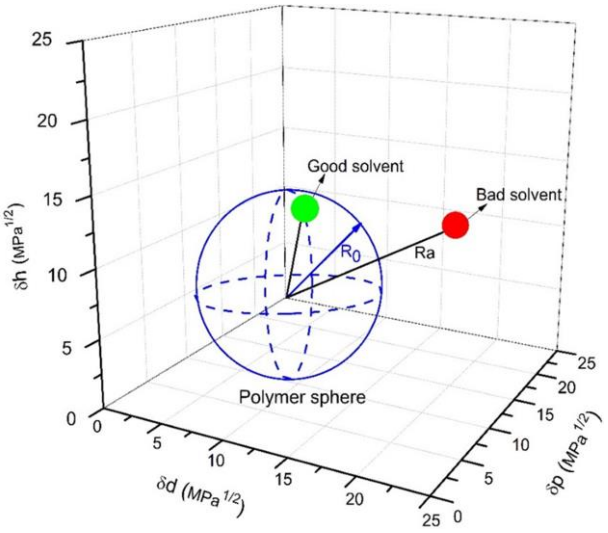

Figure 5. The radius of interaction of the Hansen solubility sphere (R_0) and the position of a good and a bad solvent for a specific polymer. [149]

TIPS is another method commonly used to fabricate membranes. The polymer is dispersed in a diluent at high temperature. Then, the homogenous dope solution is cooled to low temperature, and phase inversion is thus induced. Because of the high temperature, the polymer concentration

can be higher than in NIPS (up to 50%), leading to denser membrane surface, better mechanical strength, narrower pore size distribution, and a lower probability of defect formation compared to membranes fabricated via NIPS. In contrast, TIPS is associated with more energy consumption. The diluents mostly used in TIPS are harmful, including dioctyl phthalate (DOP), dibutyl phthalate (DBP), dimethyl phthalate (DMP), diethyl phthalate (DEP), diphenyl ketone (DPK), diphenyl carbonate (DPC), glycerin triacetate (GTA), NMP, and DMAc.

In this chapter, we discuss green organic solvents, deep eutectic solvents (DES), polyelectrolyte complexation, and solvent-free system. The HSP values of several green solvents and of typical polymers are summarized in Table 3 and Figure 6.

Table 3. HSP Values and Radius of Interaction of the Hansen Solubility Sphere (R_0) of the Polymers and HSP Values of Green Solvents.

Polymer or Solvent	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)	R_0 ($MPa^{1/2}$)	Ref.
CTA	18.4	11.9	10.1	NA[1]	[149]
CA	18.6	12.7	11	8.8	[148]
PVDF	17.2	12.5	9.2	5	[150]
PESU	19.6	10.8	9.2	6.2	[148]
PSU	19.7	8.3	8.3	8	[148]
Matrimid® 5218	18.7	9.5	6.7	NA	[151]
PVC	17.6	7.8	3.4	8.2	[148]
PAN	21.7	14.1	9.1	10.9	[148]
Lignin	20.61	13.88	15.25	11.83	[148]
Chitosan	21.9	32.5	24.6	NA	[149]

Ethyl lactate	16	7.6	12.5	-	[148, 152]
Methyl lactate	15.8	6.5	10.2	-	[153]
PolarClean[a]	15.8	10.7	9.2	-	[150, 154]
DMSO[b]	18.4	16.4	10.2	-	[155]
TEP[c]	16.8	11.5	9.2	-	[156]
γ-BL[d]	19	16.6	7.4	-	[157]
PC[e]	20	18	4.1	-	[149]
ATBC[f]	16.02	2.56	8.55	-	[157]
ATEC[g]	16.6	3.5	8.6	-	[158]
TEC[h]	16.5	4.9	12	-	[158]
TEGDA[i]	16.45	2.14	9.78	-	[159]
Cyrene[j]	18.8	10.6	6.9	-	[160]
DMI[k]	17.6	7.1	7.5	-	[161]
TamiSolve® NxG	17.8	8.2	5.9	-	[162]

Note: PolarClean[a]: methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate

DMSO[b]: dimethyl sulfoxide

TEP[c]: triethyl phosphate

γ-BL[d]: gamma-butyrolactone

PC[e]: propylene carbonate

ATBC[f]: acetyl tributyl citrate

ATEC[g]: acetyl triethyl citrate

TEC[h]: triethyl citrate

TEGDA[i]: triethylene glycol diacetate

Cyrene[j]: 1,6-anhydro-3,4-dideoxy–D-glycero-hex-3-enopyranos-2-ulose (or dihydrolevoglucosenone)

DMI[k]: dimethyl isosorbide

NA[l]: not available

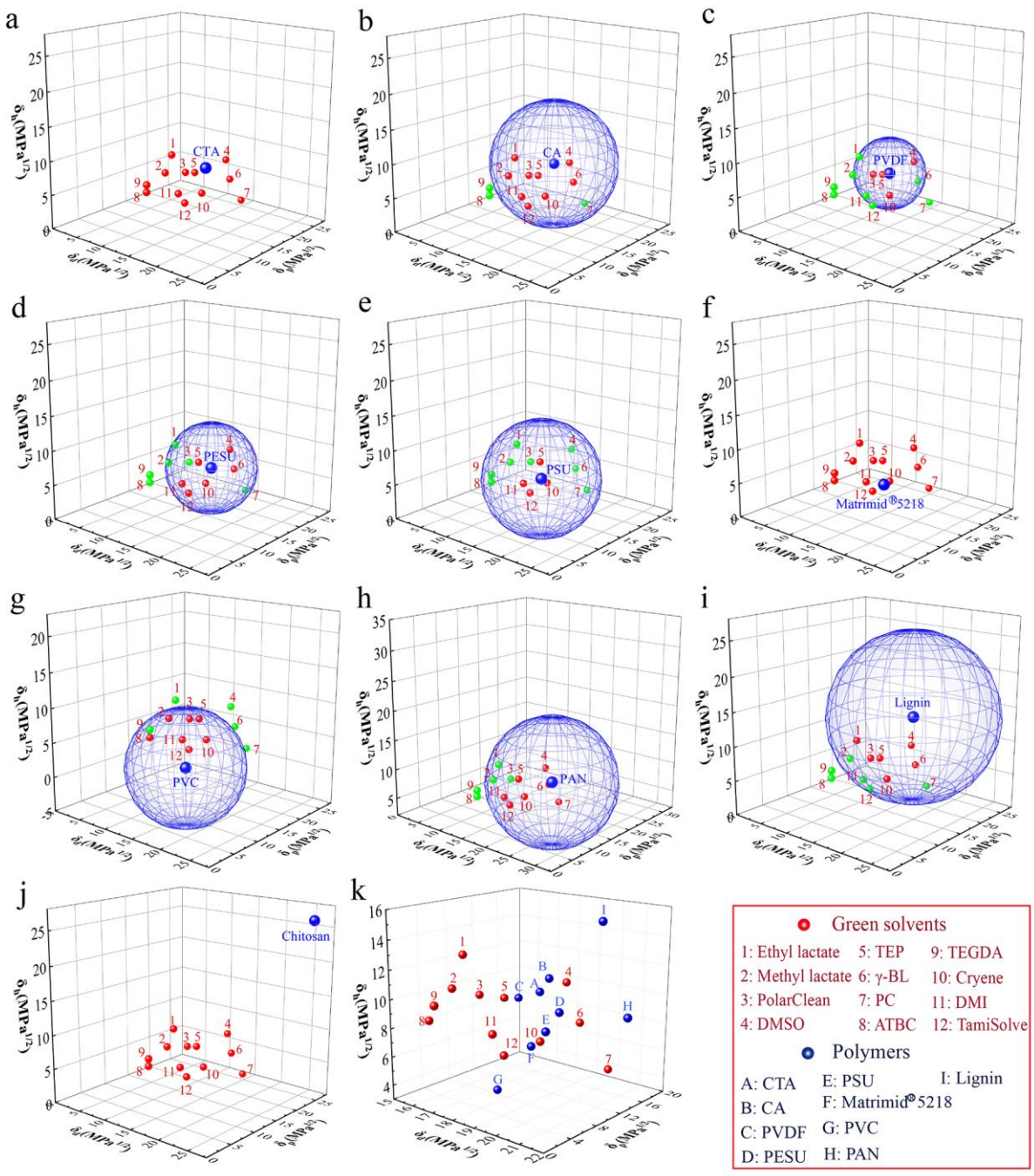

Figure 6. (b-e, g-i): Three-dimensional Hansen solubility parameter spheres of typical polymers (red dots: inside the sphere; green dots: outside the sphere). (a, f, j): Three-dimensional Hansen solubility parameters of green solvents and CTA, matrimid®5218, and chitosan (the radiuses of the Hansen solubility spheres of these polymers are not available). (k): Three-dimensional Hansen solubility parameters of all green solvents and all polymers.

Green Organic Solvents

Methyl/ethyl Lactate. Methyl lactate and ethyl lactate are lactate acid esters, which are bio-based non-toxic solvents with low vapor pressure. They can be biodegraded via the activity of hydroxyl radical by photochemical oxidation in the vapor phase. [153, 163]

Concerning membrane manufacturing, both methyl lactate and ethyl lactate are good solvents for cellulose-based polymers, such as CA. [9] The HSPs are given in Table 3. Gonzalez et al. [164] prepared CA UF membranes with LiCl as additive and methyl lactate as solvent. They evaluated the pollution potential and the ecotoxicity of this membrane, and both were determined as negligible. Further, a cellulose diacetate (CDA) UF membrane prepared with LiCl and methyl lactate was assessed via holistic metrics-based approach, considering technical, environmental, as well as health and safety (EHS) issues. Results showed that this membrane had great renewable intensity and required a low number of solvents for its preparation. [152] Moreover, CA NF membranes prepared by methyl lactate were also reported. [153] There are also some studies on the use of ethyl lactate, such as for the synthesis of tris (2,4,6-trimethoxyphenyl) phosphonium functionalized poly(2,6-dimethyl-1,4phenylene oxide) (PPO–TPQP) anion exchange membranes, [165] polycaprolactone (PCL) membranes, or PCL membranes loaded with hydroxyapatite (HA) nanoparticles scaffolds. [166]

PolarClean. Methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate (Rhodiasolv® PolarClean, abbreviated as PolarClean) is a new highly promising member of the green solvent family. This solvent is miscible with water and is derived from 2-methylglutaronitrile (MGN), a by-product in the hydrocyanation of butadiene used to manufacture adipodinitrile (ADN). [167, 168] It is completely biodegradable (97% after 18 days) with no environment and health hazards. [169] It is non-flammable and has very low vapor pressure. [169] The boiling point of PolarClean is 280 °C. According to the

Rhodia raw material database, PolarClean can reduce the carbon footprint compared to other traditional solvents.

Hassankiadeh and co-workers fabricated PVDF hollow fiber membranes via a combined NIPS-TIPS (N-TIPS) method using PolarClean as the green diluent. [169] This is the first report using PolarClean for membrane fabrication. It was found that the PVDF/PolarClean system resulted in a dense membrane structure, while additive poly(N-vinylpyrrolidone) (PVP) increased the membrane porosity. Jung et al. [150] reported PVDF flat sheet membranes fabricated with PolarClean via N-TIPS method. This membrane was modified by use of one of the following additives: Pluronics F-127, PVP, LiCl, or glycerol. The Pluronics F-127-modified membrane exhibited the highest water permeability, with values up to 2800 L $m^{-2}h^{-1}bar^{-1}$, with narrow pore size distribution. Jung and co-workers also fabricated PVDF hollow fiber membranes from PolarClean. [170] Recently, Tocci et al. [171] found the PolarClean can promote the β-phase formation of PVDF membrane.

PolarClean has good affinity with many polymers other than PVDF, and it has been used for membrane fabrication with PESU, [172] CA, [173] PSU, [173-175] PVC [154] and novel Matrimid® 5218 [151] via NIPS method. The affinity of PolarClean with these polymers is shown in Table 3. Considering its versatility, PolarClean is regarded as a promising alternative for traditional solvents. However, the multicomponent nature and multi-step synthesis of this solvent are an obstacle for its widespread use, and the price is still high (9.5 USD/kg, while traditional solvents, such as NMP or DMF, are usually in the range of 2–4 USD/kg). [172] Cseri and co-workers [176] recently proposed a more advanced and shorter synthetic route, which was more sustainable than the patented route, showing great potential in reducing costs.

Dimethyl Sulfoxide (DMSO). DMSO is a nonhazardous, biodegradable, and recyclable solvent, which is extracted from lignin or synthesized by oxidation of dimethyl sulfide. It has a high boiling point (189 °C at 760 mmHg) and a very low vapor pressure (0.6 mmHg at 25 °C). Moreover, it has good solvent power for many polymers. Until now, there have been works on CA, [177] CTA, [178] PVDF, [177, 179, 180] PAN [177, 181], PESU [23, 177, 182, 183], polyimide (PI), [184] PVC, [155] and Nafion [185] membranes fabricated using DMSO as the solvent, proving its versatility. [186] Mu and co-workers [177] fabricated PVDF, CA, PESU, and PAN microporous membranes using a simple freeze-gelation method. Moreover, Meringolo et al. [179] prepared PVDF membranes with DMSO as the solvent via a combined vapor-induced phase inversion (VIPS) and NIPS method (V-NIPS). No chemical additive was used and the resulting membrane exhibited a permeate flux up to 12.1 kg $m^{-2}h^{-1}$ with salt rejection of 99.8% in membrane distillation (MD). These tests showed comparable performance to that observed with commercial PVDF membranes.

Using DMSO as solvent, Evenepoel et al. [23] fabricated PESU UF membranes, which showed a higher permeability and rejection of bovine serum albumin (BSA) and rose Bengal (RB) compared to an analogous membrane fabricated from NMP. Prihatiningtyas et al. [178] fabricated CTA/cellulose nanocrystals (CNNs) pervaporation membranes via VIPS method, and the effect of solvents, including DMSO, dioxane, NMP, and DMF, was investigated. Among all solvents, the DMSO-based membranes resulted in homogeneously distributed CNCs on the membrane surface and a matrix with self-assembled structure.

The cost of DMSO is much lower than that of many other green solvents, and nearly at the same level of traditional solvents. It has been reported that the approximate price of the following green solvents is: 1.6 USD/kg for DMSO, 2.6 USD/kg for triethyl phosphate, 1.9 USD/kg for acetyl tributyl citrate, 19.4 USD/kg for triethylene glycol diacetate. [155]

Triethyl Phosphate (TEP). While TEP is a safer solvent for human health and worker safety compared to traditional solvents, it cannot be defined as "green". TEP is harmful when being swallowed or when in contact with the eyes. [187] Also, the use of TEP will expand the amount of phosphorus in the earth crust in the long term. [9] However, only taking into account the direct harm to people and the environment, TEP is still a better alternative to other toxic solvents. Moreover, it has a high boiling point (215 °C). [187]

TEP has good affinity with PVDF (see in Table 3), so the research on TEP has mostly focused on PVDF membrane fabrication. Karkhanechi and co-workers found that the TEP-based dope solution was more viscous than the NMP solution. Therefore, a macrovoid-free structure was observed. [188] However, Chang et al. [156] reported a more porous PVDF membrane structure resulting from a TEP-based system with respect to an NMP-based system. They prepared PVDF hollow fiber membranes with no additive for application in MD, which not only possessed robust mechanical properties but also exhibited an average flux of 20 kg $m^{-2}h^{-1}$ at a feed temperature of 60 °C, with near complete NaCl rejection. Other studies [189-192] compared PVDF membranes fabricated using TEP with other obtained with toxic solvents, namely, hexamethyl phosphoramide (HMPA), trimethyl phosphate (TMP), DMF, DMAc, and NMP, showing that TEP was a good solvent for PVDF, leading to a symmetric structure with interconnected pores. The comparison between TEP and DMSO as the solvent for PVDF membrane fabrication was also investigated, and it was found that DMSO resulted in higher porosity. [193] A combined V-NIPS method was also used to fabricate PVDF membranes with TEP as the solvent, promoting the formation of a highly porous surface.[193-196] In addition, there are some reports of fabrication of PVDF membrane via N-TIPS method. The membrane fabricated by NIPS often had numerous finger-like voids, leading to

poor mechanical strength. The combined method effectively prevented this phenomenon and promoted the formation of an interpenetrating network structure. [197]

Gamma-Butyrolactone (γ-BL). γ-BL is a non-toxic solvent with high boiling point (204 °C) and high flashing point (98.3 °C), and it can be mixed with water. Interestingly, it can easily dissociate lithium salts. [198] In industry, γ-BL is a common solvent as a superglue remover, a paint stripper, and an aroma in foods. For membrane fabrication, there have been some reports on the use of γ-BL as a non-toxic solvent. Bey et al. [199] first used γ-BL to fabricate polyetheretherketone (PEEK) hollow fiber membranes via NIPS. This membrane was successfully used for chromium(VI) removal from aqueous solutions with an extraction value of up to 99%. Polyetherimide (PEI) gas separation membranes were also prepared using γ-BL. [200] Experiments showed that PEI could not be dissolved in other green solvents, such as methyl lactate, ethyl lactate, propylene carbonate (PC), tributyl o-acetylcitrate (ATBC), tributyl citrate (TBC) and TEP, even at temperatures up to 140 °C. However, PEI was dissolved in γ-BL at 100 °C. The membrane obtained from this dope solution had a denser layer than that present in the membrane fabricated with NMP, resulting in slightly better hydrogen-methane selectivity but much lower permeability. [201]

Organic Carbonates. Stable organic carbonates are obtained from the diesterification of carbonic acid with hydroxy compounds, and their general structure is R_1-O(C=O)O-R_2. [149, 202] Their synthesis in supercritical CO_2 may be considered as environmentally friendly. The most common carbonate solvents are propylene carbonate (PC), glycerol 1,2-carbonate, and butylene carbonate. These cyclic carbonates are non-toxic, eco-friendly, and biodegradable, with high boiling points. Organic carbonates for membrane fabrication have been rarely reported. PC has been used as a diluent for PVDF membrane fabrication via TIPS. [203] Moreover, Rasool et al. [149]

studied seven kinds of organic carbonates, namely, dimethyl carbonate (DMC), diethyl carbonate (DEC), PC, 1,2-butylene carbonate (BC), glycerol 1,2-carbonate, 1,2-hexylene carbonate, and styrene carbonate (SC), to dissolve PESU, PSU, PAN, PVDF, CS, PI, CTA, and CA at room temperature. Experiments showed that CA was the only polymer that could be dissolved in carbonates BC and DMC, while other polymers were not dissolved in any of the solvents. Since the affinity of these organic carbonates and polymers were poor, traditional solvent NMP was mixed with organic carbonates for membrane preparation via NIPS. Membranes with either spongy or macrovoid structures were successfully prepared, and the filtration experiment results were satisfactory, as depicted in Figure 7.

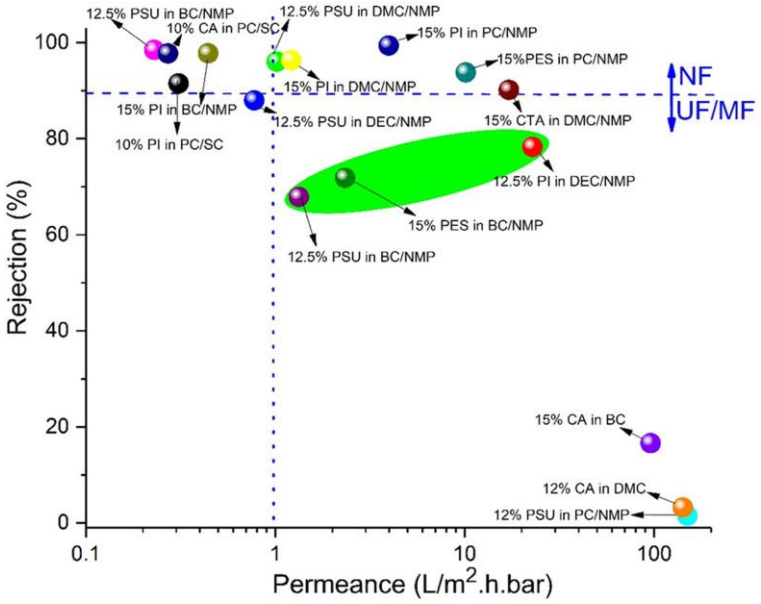

Figure 7. Permeance versus rejection of membranes prepared from carbonate-based solvents or carbonate/traditional solvent mixtures, categorizing them as either NF or MF/UF membranes. [149]

Acetyl Tributyl Citrate (ATBC), Tributyl Citrate (TBC), Acetyl Triethyl Citrate (ATEC), and Triethyl Citrate (TEC). ATBC, TBC, ATEC, and TEC, are all family members of citric acid

esters, commercially known as “Citroflex”. They are non-toxic and eco-friendly. ATBC is a widely used plasticizer in food contact polymers, medical plastics, aqueous pharmaceutical coatings, extracorporeal tubing, wraps and films, beverage tubing, and children’s toys. [204] It can be used as a diluent for PVDF UF membrane fabrication via TIPS method. Cui et al. [205] firstly used ATBC for the preparation of PVDF flat sheet and hollow fiber membranes, proving that it was a competitive and promising compound. Then, Hassankiadeh et al. [204] reported the poor mechanical strength of PVDF membranes fabricated using ATBC. Therefore, Kim et al. [206] increased the PVDF concentration up to 50 wt. %, obtaining membranes with suitable mechanical strength. ATBC was also used for poly(ethene-*co*-chlorotrifluoroethene) (E-CTFE) membrane preparation. [207] The resulting membrane possessed a spherulite structure, high surface hydrophobicity, suitable mechanical strength, promising permeate flux (22.3 L $m^{-2}h^{-1}$), and near complete salt rejection in MD.

TBC is another ester diluent used to manufacture PVDF membranes. Liu et al. [208] first reported PVDF membrane preparation using TBC, with di-(2-ethylhexyl) phthalate (DEHP) as the non-solvent. Then, Zhang et al. [209] studied the kinetics of a PVDF/TBC system with five different PVDF concentrations (30 wt.%, 40 wt.%, 50 wt.%, 60 wt.%, 70 wt.%, 80 wt.%) for four different cooling rates (5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min). It was found that PVDF took a shorter time to crystallize as cooling rate and polymer concentration increased.

As for ATEC and TEC, it is known that the solubility power to PVDF is improved in the order ATBC< ATEC <TEC, by calculation of the Hanson solubility parameter (Table 3). Sawada et al. [158] explored the effect of different diluents on the morphology and performance of the membrane. It was found that PVDF/ATEC and PVDF/TEC membranes formed spherulites, while PVDF/ATBC membranes formed only fibrillar structures. These three membranes had similar

porosity (56.1–58.9%) with average pore size in the order: ATBC (0.82 μm) < ATEC (2.88 μm) < TEC (4.29 μm).

Triacetate Ester of Glycerol (Triacetin). Triacetate is slightly miscible with water but highly miscible with alcohol and ether. It can be used as an additive in food, perfumes, and cosmetics. [9] As for membrane fabrication, triacetin has been used for PVDF membrane preparation via TIPS method. [24, 210] Ghasem et al. investigated the effects of quenching temperature, [211] PVDF concentration [212], and polymer extrusion temperature [213] on the performance of PVDF membranes for CO_2 absorption and removal. The results showed that the membrane obtained at lower quenching temperatures was dense, leading to low gas permeability. Complete removal of CO_2 was possible using a membrane contactor deploying PVDF hollow fiber membranes fabricated at high quenching temperatures. As the PVDF concentration in the dope solution increased, CO_2 flux decreased, due to a thicker and denser outer skin layer. Moreover, it was found that the PVDF membranes exhibited improved removal efficiency of CO_2 with increased extrusion temperature.

Triethylene Glycol Diacetate (TEGDA). TEGDA is not classified as dangerous to the environment, being associated with no acute or chronic effects on health. It is neither a 'PBT' substance (Persistent, Bioaccumulative and Toxic) nor a vPvB substance (Very Persistent and Very Bioaccumulative). [159] TEGDA is generally employed as a plasticizer, and only one report can be found of its use as a low toxic diluent for PVDF membrane fabrication via TIPS method. [159] The crystals of this PVDF membrane were α phase and a specific fibrillar structure was formed, which yielded PVDF membranes with high elongation and permeability properties.

Dihydrolevoglucosenone (Cyrene™). Cyrene™, or 1,6-anhydro-3,4-dideoxy–D-glycero-hex-3-enopyranos-2-ulose, is a sugar-based solvent derived from cellulose. [160] The synthesis route only contains two steps, as depicted in Figure 8a, ensuring atom economy and low environmental

impact. Also, there are no nitrogen or sulphur heteroatoms in Cyrene™, which prevents NO_x and SO_x emissions upon incineration. Moreover, it is non-toxic, and it has high boiling point (227 °C) and high flashing point (108 °C) at 760 mmHg, with very low vapor pressure (0.28 Pa at 25 °C). Cyrene™ is considered as a prospective green alternative to traditional solvents NMP, DMAc, and DMF in membrane fabrication process, due to similarities with these compounds in terms of solubility parameter, polarity, density, and miscibility with water.

Marino et al. [214] employed Cyrene™ for the first time to manufacture PVDF and PESU membranes via V-NIPS method. Without any pore forming agent, a short exposure time (0-5 min) to relative humidity of 55% achieved tunable pore sizes from 0.55 µm to 0.03 µm (PVDF membrane) and from 0.12 µm to 0.02 µm (PESU membrane). Therefore, the pure water permeability could also be controlled. This work identified the feasibility of Cyrene™ in the fabrication of water treatment membranes. A recent study found that Cyrene™ is capable of dissolving PVC and CTA at 60 °C, but the resulting polymer inclusion membranes (PIMs) were inhomogeneous and opaque, exhibiting different appearances from those fabricated from traditional solvents. However, they worked adequately for Zn(II) extraction. [215] Cyrene™ is a promising green solvent for membrane manufacturing, but only two research works have been reported, and more efforts to improve its applicability are encouraged.

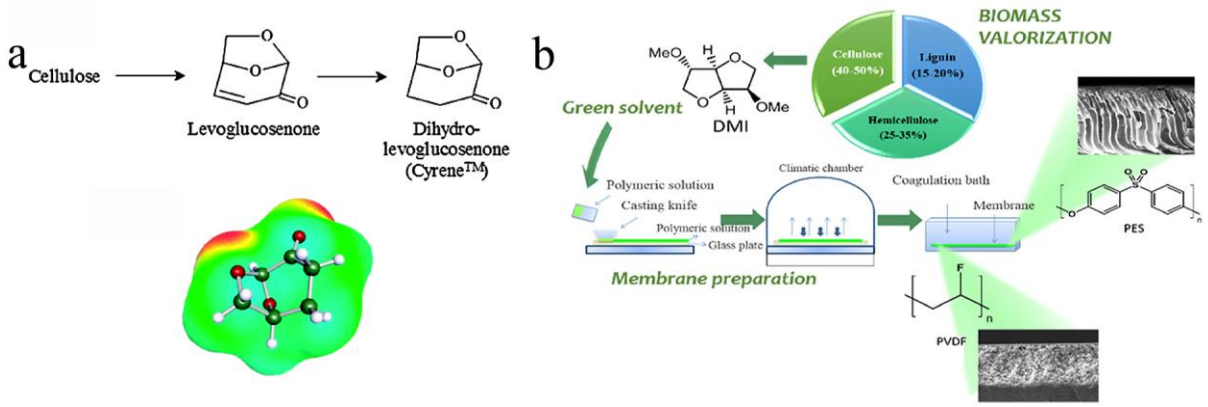

Figure 8. (a) Scheme for the production of Cyrene™ and its σ-surface (COSMO surface). [160] (b) Dimethyl isosorbide as a green solvent for PVDF and PESU ultrafiltration and microfiltration membrane preparation via N-VIPS method. [161]

Dimethyl Isosorbide (DMI). DMI is another sugar-based green solvent, synthesized via methylation of the anhydro sugar isosorbide or directly derived from D-sorbitol, which is ranked in the top-10 biobased platform chemicals. [216] DMI is non-toxic and water-soluble with high boiling point of 235-237 °C at 760 mmHg. [161] Russo et al. published the only research so far on DMI for membrane fabrication. [161] They confirmed that DMI possess the required physical/chemical properties to cast PVDF and PESU membranes in terms of Hansen solubility parameters, relative energy difference, and viscosity. Membranes were manufactured via V-NIPS method without any pore forming additive: porous structures with a tunable pore size in the range of UF and MF could be obtained by controlling exposure time to humidity. The process is depicted in Figure 8b. DMI is a new green solvent with a bright future in membrane preparation strategies.

TamiSolve® NxG. TamiSolve® NxG is a non-reprotoxic and biodegradable solvent. It exhibits similar properties of traditional organic, polar aprotic solvents for membrane fabrication, such as NMP. TamiSolve® NxG has been used for poly(vinylidene fluoride-hexafluoropropylene) P(VDF-HFP) membrane fabrication for use in direct contact membrane distillation (DCMD), showing comparable performance to commercial PP membranes. [162]

Deep Eutectic Solvents (DESs)

In 2003, Abbott et al. [217] first published a paper on DESs as an alternative option to ionic liquids (ILs). DESs consist of a mixture of organic compounds, and comprise strong hydrogen bond

interactions between suitable hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs). [217, 218] They share many properties with ILs (*e.g.,* low melting point, low vapor pressure, and high thermal stability), but they are less toxic, more biodegradable and eco-friendly, and associated with lower costs. [219] In addition, they possess the additional features of ease of preparation, 100% atom economy, extensive tunability, and universal dissolution abilities. [220] A large number of HBAs and HBDs are available to prepare DESs (Figure S3, SI). Among them, the top candidates are choline chloride (ChCl) and urea for HBA and HBD, respectively.

The environmental impacts of DESs have been investigated in terms of biodegradability and toxicity. Taking into consideration the properties of singular components of DESs, DESs should more biodegradable and lower toxic than ILs. Cholinium-based DESs suffered a degradation of up to 80% after 21 days. [218] Meanwhile, the toxicity of DES was found to be dependent on its composition and concentration. It was reported that cholinium-based DESs has a greater cytotoxic effect than their singular components. However, the authors observed no toxic effect on the studied bacteria. [221] Overall, DESs are greener solvents than ILs in terms of environmental, as well as health and safety (EHS) impacts.

Recently, the applicability of DESs has been explored in membrane technology, mainly focusing on using DESs as additives, as surface modifiers, or for liquid membranes fabrication. Jiang Bin et al. [222] [223] first used DESs as additives in membrane casting solutions for PESU UF membranes fabrication. They found that DESs played a role as pore forming agents rather than as surface modifiers. A small amount (2 wt.%) in the casting solutions greatly enhanced the water permeability values, but the anti-fouling properties of the membranes were not improved. Recently, Seyyed Shahabi et al. [224] added a choline chloride-urea based DES to the MPD aqueous solution to modify the PA layer of RO membranes during synthesis via interfacial polymerization. They

observed a smoother surface, enhanced water flux and salt rejection, with respect to membranes obtained without DES. Maalige et al. [225] reported three different choline chloride-based DESs as surface modifiers for surface treatment and cleaning of thin-film composite polyamide membranes (TFC-PAs). The enhanced surface wettability and surface smoothness of the DES-treated membranes resulted in remarkable increases in the flux rate and flux recovery without substantial changes in the solute rejection efficiencies. This phenomenon was attributed to the presence of H-bonding between DES and PA moieties. DESs have also been investigated for liquid membranes fabrication. [226-228] They were imbedded into the pores of a solid porous framework via immersion or pressure impregnation. These liquid membranes may be used for efficient CO_2 separation, ethylene/ethane separation, or fuel cell application on account of their enhanced proton conductivity.

However, to the best of our knowledge, DESs have never been investigated as the main solvents to prepare membranes. The Hansen solubility parameters of ChCl-based DESs are depicted in Table 4, translating into a relatively far distances from polymers materials (seen in Table 4). Therefore, maybe such specific DESs do not have good solvent power to typical polymers. However, given that the properties of DESs can be easily tuned by changing the HBD and HBA components, there may be combinations resulting in mixtures that would dissolve polymers for membrane manufacturing. Whether this proposal is feasible, however, remains to be explored.

Table 4. The Average Molar Mass (M_{ave}) and Hanson Solubility Parameters (δ_t) of Choline Chloride-based DESs. [229]

HBA	HBD	HBA: HBD (molar ratio)	M_{ave} (g/mol)	δ_t ($MPa^{1/2}$)

choline chloride	urea	1:2	86.57	31.8
choline chloride	ethylene glycol	1:2	87.91	29.1
choline chloride	glycerol	1:2	107.93	31.5
choline chloride	Malonic acide	1:1	121.84	35.6
choline chloride	Oxalic acide	1:1	114.83	33.4

Polyelectrolyte Complexation Induced Aqueous Phase Separation

Water is the greenest and most abundant natural solvent in the world. The possibility to utilize water as both solvent and nonsolvent for membrane fabrication has attracted considerable interest. Traditional polymers, for example, PVDF, PVC, PESU, PSU, cannot dissolve in water. Polyelectrolytes (PEs) are charged polymers with either positive or negative charges on their repeating units, surrounded by small counter-ions, which stand out due to their water solubility. When two oppositely charged polyelectrolytes are mixed, they can form a water-insoluble solid known as polyelectrolyte complex (PEC), which can be cast as a thin film. Sadman et al. [230] used the coacervate of anionic poly(styrene sulfonate) (PSS) and cationic poly(N-ethyl-4-vinylpyridinium) (QVP-C2) dissolved in KBr solution to form a complex coacervate. The behavior of the complex in highly concentrated KBr was exploited to form membranes with porosities ranging from nanometers to micrometers of size using water-water phase inversion via immersion precipitation in a low ionic strength solution (the schematic is shown in Figure S4, SI). Recently, Baig et al. [231] reported a similar approach by using water solutions with different pH values. They prepared a homogeneous solution of the strong polyanion PSS and the weak polycation poly(allylamine hydrochloride) (PAH) at high pH, whereby PAH is not charged (pKa ~ 8.8). The solution was cast and immersed in a low pH bath to charge the PAH and resulted in controlled

precipitation, forming a porous water-insoluble PEC membrane. By tuning parameters, such as PE concentration and molecular weight, the membrane pores can be tuned from MF, UF, to NF. This novel membrane fabrication process eliminates the use of organic solvents and the membranes can be cast with tunable pore size ranging from MF to NF. However, this process still has some drawbacks. Extensive time and cumbersome protocols are needed for solution preparation and for the following coagulation process, thus impairing mass production.

Solvent-free Systems for Hydrophobic or Hollow Fiber Membrane Manufacturing

Melt spinning and cold stretching (MSCS) is regarded as the simplest membrane fabrication method given that it does not involve any phase inversion process. During this process, the polymer melt is spun at a temperature close to its melting point and then the micropores of the membrane are formed by the mechanical force acting on the material in a subsequent cold-stretching step. [232] Because no solvents or additives are required, this method is both economical and clean. However, the membrane fabricated by MSCS usually suffer from poor filtration performance and membrane fouling problems. To address these issues, Ji et al. [233] used poly(ethylene oxide) (PEO) as pore forming agent and melted it together with PVDF, obtaining a membrane with tunable pore size and tensile strength. The mean pore size of the prepared membranes with 100% stretching was about 0.317 μm, which showed a high dye rejection (< 93.9 %) for Direct Black 19. On the basis of the MSCS method, some new ideas have emerged: melt/solution integrated homogeneous-reinforcement method, homogeneous braid reinforced hollow fiber membranes, melt spinning-stretching interfacial phase separation method, and nanofibers-covered hollow fiber membranes via continuous electrospinning, which should improve the membrane performance while also relying on the sustainability of the process. [232]

The methodologies discussed above can also be undertaken for hydrophobic membrane fabrication. In the very next future, engineers will produce more hydrophobic porous membranes for novel membrane operations, such as membrane distillation, membrane crystallizers, membrane contactors. It might be more complicated to consider the appropriate green solvents and polymers than in the case of hydrophilic membranes. Solvent-free methodologies might be useful for their large scale productions. However, the massive energy required to melt the polymers should be considered.

Challenges and Outlook

In the European Union, the use of NMP has been restricted. The regulations state that, as of May 2020, NMP can no longer be used in a concentration above 0.3%, unless the manufacturers and consumers take appropriate risk management protocols. It is obvious that a similar fate awaits other traditional solvents with environmental and health risks. Therefore, it is urgently important to substitute traditional solvents with greener ones in the chemical industry, including the membrane manufacturing processes. However, this substitution must be based on two conditions: i) the membrane performance is not impaired and, if possible, it is improved; ii) the price of green solvents is competitive. Some research has clearly shown that both goals are achievable simultaneously. A membrane performance comparison when applying green solvents or traditional solvents is summarized in Table S2 (SI), indicating competitive and even better performance when green solvents are used. Cseri et al. [234] reported that there is no direct correlation between the sustainability and the price of solvents. Replacing a traditional solvent with a greener alternative may thus be cheaper in some cases. Another important factor is that life cycle assessment (LCA) is needed to compare "green" and traditional membranes. The production, use, and disposal phases all need to be assessed, with detailed statistics of environmental impacts. This LCA method may

provide a robust comparison between traditional and green solvents, and illustrate when the use of green solvent would indeed reduce the environmental impacts of the membrane.

SOLVENT WASTEWATER TREATMENT AND RECYCLING

Wastewater is an inevitable problem during the membrane preparation processes, especially those based on NIPS method. It has been reported that 100–500 L of wastewater is generated per square meter of membrane, and the contamination in wastewater generally exceeds the minimum allowable level of 100 ppm. Therefore, treatment is required before disposal. However, the reality is that over 69% of the wastewater produced by membrane fabrication factories is discharged without effective treatment. [19] This wastewater generally contains organic solvents and a small amount of additives and polymers. Its direct discharge endangers aquatic life and damages the ecosystems, seriously reducing the sustainability of membrane technology. If the wastewater were to be treated effectively, the in-house reuse could be accomplished, and the concentrated organic solvents could be recycled. However, purification should be accomplished with low price and high efficiency.

To date, there have been few reports presenting organic wastewater treatment from the membrane fabrication process. Razali et al. [19] used adsorption and seven different classes of adsorbents, namely, graphene, polymers with intrinsic microporosity, molecularly imprinted polymers (MIPs), zeolites, metal organic frameworks, activated carbon, and resins, to remove NMP or DMF from membrane industrial wastewater. Results showed that most adsorbents exhibited feasible performance to treat the membrane wastewater, and over 99% of the organic impurities in the wastewater were successfully removed; the recycled water may be reused without adverse effects on the performance of the membranes. Meanwhile, the adsorbent regenerability

was confirmed for up to 10 wastewater treatment cycles. This is an effective technology with low price, applicable in the membrane fabrication process. In another study, the wastewater was treated by membrane filtration, and both the extracted resource and water were recycled into membrane fabrication process. [233]

THE APPLICATION OF ARTIFICIAL INTELLIGENCE IN MEMBRANE TECHNOLOGY

In recent decades, artificial intelligence (AI) technology and related in silico fields have developed rapidly and made important breakthroughs. Membrane scientists have started applying AI to membrane preparation as well as membrane operation for the purpose of optimizing the processes and their improving efficiency.The major challenge in these efforts is the lack of a reliable model predicting the influence of the preparation parameters on the resulted membrane performance. [235]Different interconnected parameters affect the membrane performance simultaneously and in a complex way. This issue requires designers having a systematic knowledge of the field as well as available data about the various parameters relative to membrane fabrication (*e.g.*, polymers, solvents, additives, temperature, humidity), and those relative to the final membrane performance. Also, AI is based on big data analysis. Therefore, compiling as much data as possible and finding meaningful correlations of the complex and multi-dimensional system is of vital importance to modeling and model domestication.

There have been some breakthroughs in this field recently. Zhou et al. [236] used models to evaluate the performance of 12,723 MOF adsorbents or membrane materials from the CoRE 2019 database for D_2/H_2 separation. The subsequent machine-learning methods enabled predictions of novel nanoporous materials features. Rall et al. [235] used artificial neural networks and machine-

learning techniques to realize the simultaneous optimization of the membrane and the separation process relative to layer-by-layer NF membrane modules. Other works utilized AI for performance prediction of organic solvent nanofiltration membranes [237] as well as for PVDF, PESU, PSU micro/ultra/nano-filtration membranes. [238] AI technology and related in silico fields have great potential to improve the efficiency of membrane technology, coupling the membrane fabrication step with the design of the membrane processes. There are possibilities for exploration, and to push artificial intelligence in the realm of membrane technology.

END-OF-LIFE MANAGEMENT OF SPENT MEMBRANE MODULES

Membrane elements have limited lifetime. For RO membranes, it is typically 3-7 years, while for MF and UF membranes, it is usually 7-10 years. [1] For gas separation membranes, the lifetime is much shorter due to their exposure to harsh conditions. Therefore, large quantities of membrane elements are discarded annually. Specifically, over 14,000 tons of RO membrane modules are disposed of every year, while for UF and MF membranes this number is even higher. For hemodialysis, over 600,000 tons of potentially hazardous dialyzer waste is produced every year, while the waste from gas separation activities is about 10 times less than that from RO operations. [1, 30] All these numbers are unceasingly increasing.

Although faced with a tremendous amount of waste, engineers have paid little attention to the end-of-life management and the environmental impact assessment of membrane modules. [1] Usually, the solid wastes are disposed in landfills or by incineration, but both treatment methods pose risks to the environment. The waste management hierarchy of the European Directive 2008/98/EC (Figure 9a), proposes the priorities and the most sustainable strategies for the

management of spent membrane modules. The CO_2 emissions and resource depletion for each strategy are summarized in Figure 9b.

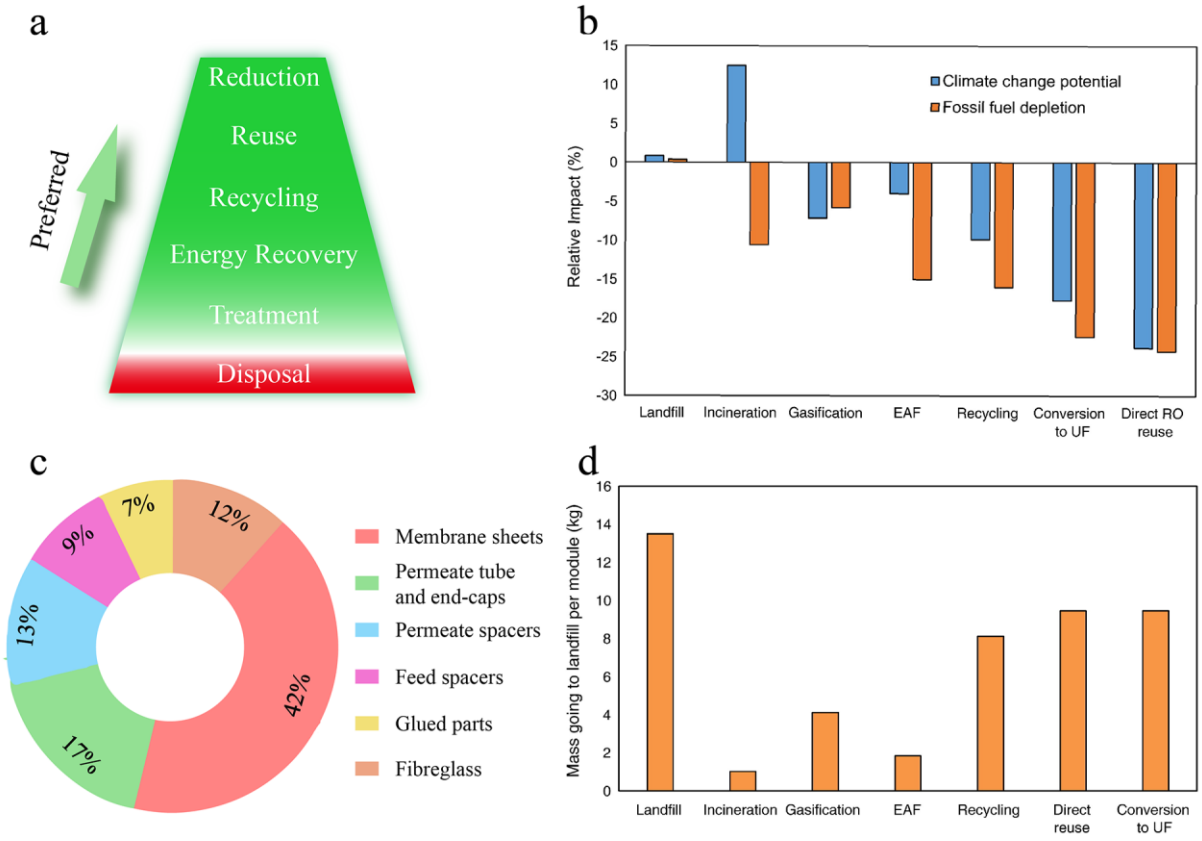

Figure 9. (a) Waste management hierarchy from most to least preferred options. [239] (b) Greenhouse gas emissions and resource depletion for the disposal of one RO membrane element. [240] (c) Composition of a typical RO membrane element [239] and (d) mass of waste material requiring landfill disposal for each of end-of-life scenarios for one RO membrane. [240]

Reduction

Reducing the amount of wasted membrane elements is the first priority, and several approaches can be taken to this purpose. Firstly, the membrane should be made with high performance, including suitable mechanical property, superior anti-fouling properties, and minimal aging or swelling. These characteristics would ensure a relatively long lifetime. Secondly, the choice of

daily operational parameters is important and membrane lifetime can be extended under lower transmembrane pressure and mild conditions. Daily maintenance is also critical to rapidly identify damaged fibers and repair them in time. Thirdly, as detailed in Bio-based Polymers for Membrane Manufacturing, bio-based materials can be included into the membrane manufacturing process to replace petroleum-based ones, with the goal of biodegradation after disposal, thus reducing the ultimate amount of solid waste.

Spent Membrane Reuse

The reuse of membrane elements means their direct application in lower throughput systems. Although a spent RO membrane usually no longer satisfies the initial selectivity criteria, it can still maintain more than 96% rejection rate, and it may be applied in seawater pretreatment or selective demineralization of brackish water. Direct RO reuse has both the greatest reduction in CO_2 emissions and fossil fuel depletion among all strategies (Figure 9b).

Membrane Element Recycling

Recycling of RO membranes includes direct recycling and indirect recycling. Direct recycling means the chemical conversion of RO membrane into NF or porous UF membranes. [241-243] Most RO membranes are composed of a thin and dense PA layer, a thicker porous PSU layer, and a non-woven polyester backing layer. By controlled degradation of the PA layer, RO membranes may be converted to NF or UF membranes. It was reported that the best chemical agent to degrade PA layer is sodium hypochlorite (NaOCl): the exposure level (ppm·h) determines the permeability and rejection of the resulting membrane. [241] Potential applications for the converted RO membranes are in pre-treatment filtration for desalination, advanced treatment of wastewater, and freshwater production in rural zones. [244] According to Figure 9b, this conversion is only slightly

worse than RO reuse method in terms of sustainability, due to the extra chemical treatment steps involved.

Indirect recycling means mechanical and chemical recycling of all plastics of membrane elements, containing not only PA, PSU and polyester, but also PP for the feed spacer, polyester for the permeate spacer, acrylonitrile butadiene styrene (ABS) for the permeate tube and end-caps, fibreglass for the outer casing, and glued parts containing proprietary epoxy-like components. The composition of a typical RO membrane is shown in Figure 9c. All these materials may be extracted and recycled via diverse recycling routes, such as mechanical recycling and chemical recycling (recycling to monomer). [245]

Energy Recovery

If or when reusing and recycling markets cannot absorb all membrane waste, energy recovery could be a valid solution to provide heat energy for electricity generation or other heat-related processes. [246] Incineration, syngas production, and electric arc furnace (EAF) are categories of energy recovery. Incineration is the most convenient for electricity generation. However, because of lack of selectivity, pollutant emissions in the gas stream may be very high, especially in terms of dioxins and fly ash, as well as considerable CO_2 emissions. The gasification process provides greater environmental benefits compared to incineration, owing to electricity production through the combustion of the generated syngas. [239, 246] The third energy recovery approach involves the use of the membrane material as polymeric carbon source in EAF for steelmaking, to reduce the use of metallurgical coke. [240]

Waste Materials Requiring Landfill

The waste materials include components that cannot be treated (*e.g.*, the fiberglass in EAF), and the residue waste generated from the recovery, recycling, or treatment processes themselves (*e.g.*, slag from the gasification and incineration processes). These waste materials need ultimately to be landfilled, and the mass of waste for each end-of-life strategy is demonstrated in Figure 9d. Although membrane reuse and recycling provide prominent environmental benefits, they will still produce large amounts of waste requiring eventual disposal. Therefore, if the absolute priority is the aversion of waste from landfills over all other impacts, incineration, or better, incineration following reuse/recycling remains the best option.

Challenges and Outlook

End-of-life membrane management is crucial to transform a traditional linear process to a circular process. Different strategies may be adopted, while landfill is the worst one in terms of environmental effects. However, when it comes to the mass of waste requiring landfill, incineration generates the least amount of mass, while membrane reuse alone is associated to the second largest after direct landfill. Therefore, the best scheme for end-of-life management needs to combine the actual situation and the final demand. Obviously, obtaining both economic gains and environmental benefits is the ideal goal. In this process, life cycle assessment (LCA) is useful to compare the different options quantitatively and to identify the optimal scheme.

However, current reports on membrane elements end-of-life management are limited, and the few that are available all focus on RO membranes, neglecting other membrane types. Facing with the continuous growth of discarded membrane elements, we should take more efforts to conduct research of their end-of-life management and promote practical applications of the spent modules, thus greatly increasing the sustainability of the membrane industry.

CONCLUSIONS AND FUTURE PERSPECTIVES

When confronted with increasingly serious energy crisis and environmental pollution, green chemistry and green engineering may provide important help in our endeavor to overcome these challenges. The Principles of Green Chemistry advocate the use of renewable materials and production processes with lower impact on the environment. Membrane technology has been implicitly considered as a green and sustainable technology. However, starting from membrane manufacturing all the way to membrane disposal, there are problems that negatively affect the sustainability of this industry.

The use of petroleum-based polymers as membrane materials is related to a series of environmental issues, and bio-based polymers are feasible options to improve membrane sustainability. However, some drawbacks currently hinder the deployment of biopolymers, such as poor mechanical properties, long running instability, and high costs. There is no doubt that further research is needed to master membrane preparation using bio-based materials while simultaneously achieving comparable or even superior performance with respect to current petroleum-based membranes. Bio-based membranes may be more readily applied in the medical fields and other fields that are not impaired by microbial degradation.

The utilization of green solvents to substitute current toxic ones is another important strategy to improve the sustainability of the membrane manufacturing process. However, environmental advantages alone most likely cannot enable the widespread adoption of green solvents, and other factors related to performance, health, and cost should also be taken into account. Therefore, identifying suitable green solvents for membrane fabrication is a challenge. More sustained studies are needed to identify alternative solvents and exploit their advantageous properties in membrane manufacturing. Given the fact that there are still challenges to the effective application of green

solvent alternatives, the treatment and recycling of organic solvent wastewater may be a viable approach to reduce pollution. If the wastewater is treated effectively, the reuse of wastewater may be accomplished, and the concentrated organic solvents may be recycled. However, reports in this field are very limited, and more research is urgently needed to find ways to purify the wastewater at low price and with high efficiency. AI technology and related in silico fields have great potential to improve the efficiency of membrane fabrication and operation,. The literature in this field is emerging, and we believe that more efforts can push artificial intelligence in the realm of membrane technology.

The end-life-management of spent membrane elements is another important issue of great concern. The reduction, reuse, recycling, and/or energy recovery of used membrane elements, rather than their direct landfill or incineration, should be pursued to drive membrane technology into a circular economy approach.

That being said, quantification of the real impacts of new materials or processes and evaluation of their sustainability are complex analyses, and a complete LCA, including the production, use, recycling, and disposal phases should be established to consider the real burdens related to membrane technology. One cannot judge whether a solvent is greener or not merely considering one or a few metrics. LCA can more robustly inform as to which raw materials or processes contribute the most impacts; engineers should thus target those to rapidly reduce the associated problems, by applying the strategies that are found to contribute the most to reduce such impacts. An important limitation is that the necessary data and information to perform robust LCA studies are difficult to obtain, both in databases or from experiments, and progressively better and more appropriate databases should be established.

In the future, the definition of membrane performance should be expanded, including sustainability considerations. This transformation requires the innovation of science and technology coupled with new emerging systems thinking and systems design, resulting in a positive impact on a global scale.

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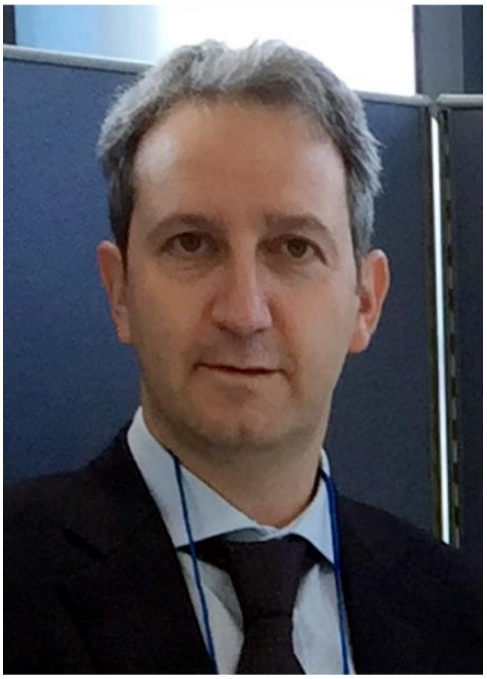

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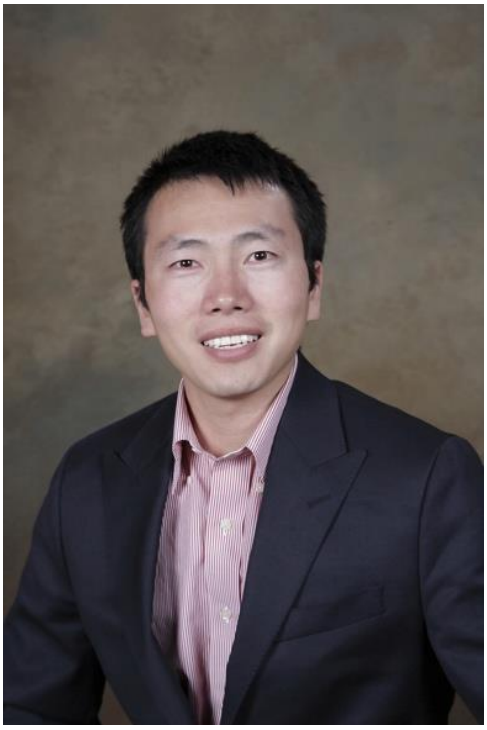

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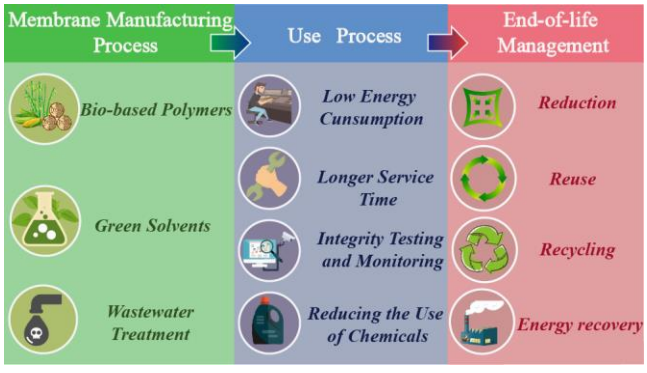
GRAFHIC ABSTRACT



SYNOPSIS

Recent advances in methods for increasing the sustainability of membrane technology, covering membrane manufacturing process, use process and end-of-life management.