

Green solvents for membrane manufacture: Recent trends and perspectives

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Abstract

Membrane fabrication highly relies on solution processes. Environmental and health concerns are driving the investigation of alternative green solvents to substitute classical toxic ones. Recent contributions to this topic are reviewed, comparing advantages and drawbacks of manufacturing membranes using water, bio-sourced solvents, non-toxic synthetic organic solvents and ionic liquids as the most explored.

Introduction

Environmental awareness and health concern have driven strict recommendations of emission control in the industry and other sectors directly affecting our lives. There is an urge to implement zero-emissions of greenhouse gases in 2050 in an attempt to stop or revert the global temperature increase. Carbon capture alone is not sustainable enough. It is essential to act in advance. Sustainability in industrial processes and a holistic foresight are needed. There is a recognized need for actions to conserve our natural capital of fresh water, clean air and the biodiversity and pollution minimization is essential for that. Membrane technology has a great opportunity to become a crucial tool toward process intensification in sustainable chemical and pharmaceutical industries, as well as toward sustainable water purification and reuse. Their contribution to water desalination and reuse is undeniable and extending their application to industrial separations could save great part of the energy demanded by traditional unit operations like distillation. Membranes could be particularly attractive in designing greener continuous processes of separation for dehydration, in-line concentration, crystallization and pharmaceutical drugs purification. [1]

However, beyond the contribution to the environmental and economic improvement of separation processes, the membrane manufacturing industry itself needs to be part of the

transition. Reviews on the sustainability of nanomaterials and chemical processes [2], green membrane manufacture [3] have been recently published. Bio-based and biodegradable polymers [4] are among “green” materials. Derivatives of natural polymers have been used since the introduction of membrane-based separations. However, processing materials such as cellulose in solution for many years required harsh solvents. Working with large scale recyclable polymers is a possibility, [5] as long again as the processing itself is green. Conversion/recovery [6] of polymer materials is of increasing importance and we ideally should come with solutions that permit a full cycle of circular chemistry for membrane materials production, as well as recycling methods for module transformation and reuse. Nevertheless, reducing the exposure of workers to harmful chemicals in the production is an important point.

This review is specifically focused on recent trends in green solvents as strategy for sustainable membrane fabrication. Most commercial polymeric membranes are produced by solution processes such as non-solvent induced phase separation (NIPS) or by thermal induced phase separation (TIPS), which also includes solvents. Unfortunately, widespread solvents in the membrane industry, such as N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAc) and N-methyl pyrrolidone (NMP) are considered substances of very high concern (SVHC) and toxic to reproduction. Special authorization is currently needed for their use in the industry and restricted conditions apply. For instance, in Europe, the regular long-term (8h daily) exposure to DMF or DMAc needs to be lower than 15 mg/m^3 ; for NMP is 40 mg/m^3 , hexane 72 mg/m^3 , toluene 192 mg/m^3 , methanol 260 mg/m^3 , cyclohexane 700 mg/m^3 . This has motivated the search for alternative green solvents for membrane fabrication. The awareness is slowly growing. The number of publications on “green solvents for membranes” evolved in the Web of Science from 5 to above 200 per year in the last 20 years. A more specific distribution of publications on current green solvent approaches for membranes is shown in Figure 1, with the expected advantages of each one of them. A green solvent is expected to be non-toxic, non-volatile, and/or derived from renewable sources.

Membrane production without solvents

Ideally, processes of membrane manufacture without solvents could be the most environmentally beneficial technologies. However, membranes have been produced for several decades mostly by

solution processes. Reverse osmosis and nanofiltration membranes are mainly produced by non-solvent induced phase separation (NIPS) as integral asymmetrically porous or as thin-film composite (TFC) membranes, prepared by interfacial polymerization (IP) coating, all steps requiring large amount of solvents. Substituting these technologies by another one without solvents, keeping similar surface area production rate would not be realistic at this moment. However, technologies without solvent are already available for diverse applications. Well-established is the preparation of microfiltration membranes from semi-crystalline polymers such as polytetrafluorethylene, polyolefin and poly(vinylidene fluoride) (PVDF) by extrusion followed by stretching. A growing expectation is toward micro- and nanofabrication methods, such as 3D printing. The resolution of the method for ultrafiltration (UF) porous membranes is still not high enough, but the method progresses fast and it is expected that it will soon be more applied for membranes. [7] 3D printing is being used also for ceramic and might open perspectives for more versatile and cost-effective process for this class of materials. [8] Resolution is here an important factor, as well. Isoporous membranes with pore size down 700 nm have been recently manufactured without solvents, using a combination of photolithography and dry reactive ion etching. [9] The method for lower pore sizes is being currently optimized.

Membrane production using green solvents

Membrane production using water

The most convenient solvent would be water. Some recent developments are listed in Table 1. An innovative method has been introduced by the de Vos's group [10-11] on the membrane preparation using water as casting solvent. The phase separation and pore formation are mainly driven by changes in pH. It is a very attractive concept, since water would be the greenest solvent. A similar procedure using water as solvent and promoting phase separation by altering the ionic strength has been proposed by the Wessling's group. [12] The methods have a broad potential. Stability might be an issue to improve. These methods applied to a relatively restrict class of functionalized polymers in a certain window of conditions. Further development of methods based on aqueous solutions would be very beneficial.

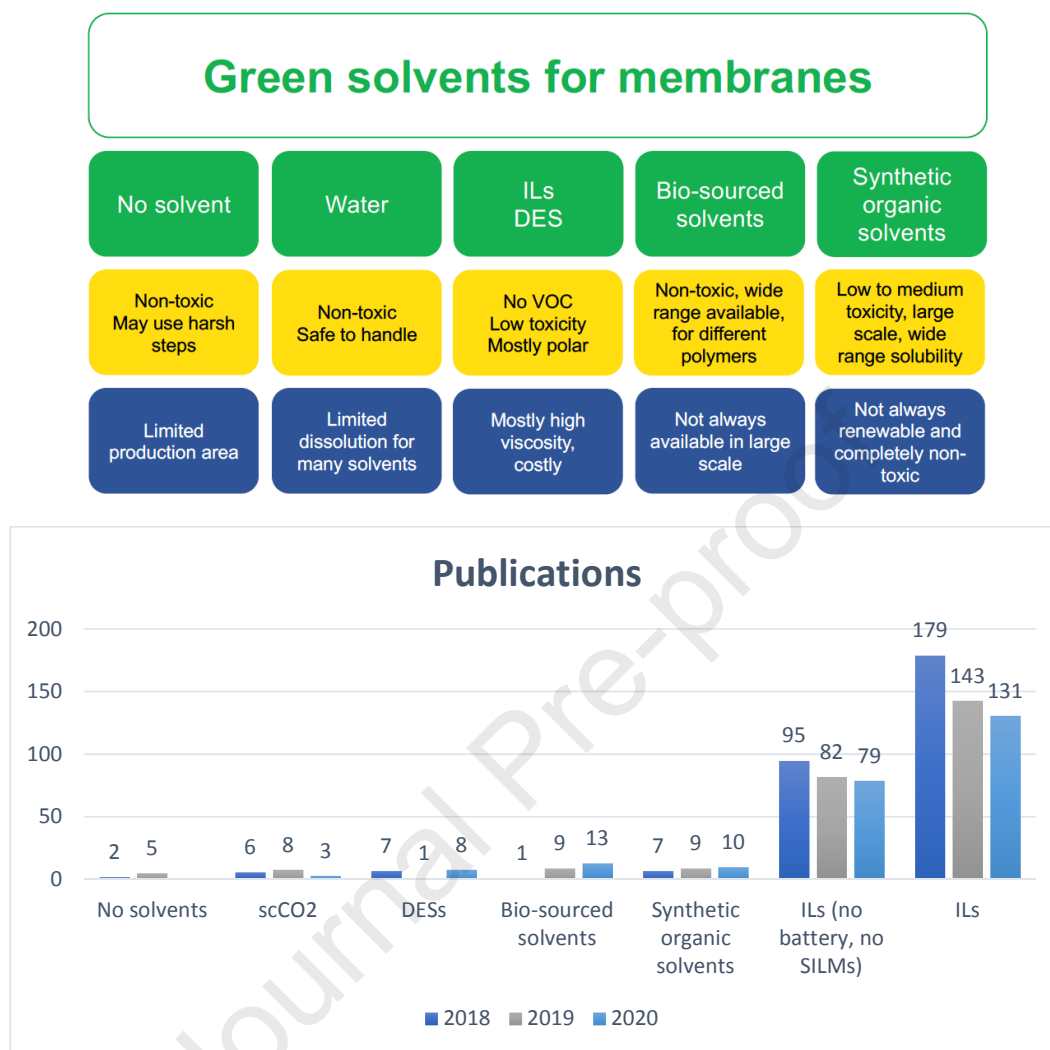


Figure 1. Key properties, safety of green solvents used for membrane production, and publications count from 2018 to 2020 in Scopus strictly linked to the corresponding solvents applied to polymeric membranes.

Table 1. Water and bio-sourced solvents for membrane manufacture.

Solvent	Polymer	Method	Process	Ref.
Water	PSS/PAH	Aqueous phase separation (APS)-pH induced phase separation	NF/MF	[10-11]
	PSS/PDADMAC	Salt induced phase inversion	NF/UF	[12]
	PSS/QVP-C2	Salt induced phase inversion	UF	[13]
	Sodium Alginate	Dip-coating	NF	[14]
Bio-sourced solvents				
Methyl lactate/2-methyl tetrahydrofuran	CA	NIPS	NF	[15]
Coconut oil (Decanoic acid)	Modified PA	IP	NF	[16]
γ -Valerolactone	PSU	NIPS	UF	[17]
γ -Valerolactone and glycerol deriv.	Various	NIPS	NF-MF	[18]
Cyrene	PES, PVDF	NIPS/VIPS	UF/MF	[19]
Isosorbide	PVDF, PES	NIPS, NIPS/VIPS	UF/MF	[20]
N,N-dimethyl lactamide	PES	NIPS	UF	[21]
Succindiamide	PVDF, PES, PAI	NIPS	Not tested	[22]
Glycerol deriv./2-MeTHF	CA	NIPS	NF	[23]
Dimethyl isosorbide (DMI)	PVDF, PES	VIPS/NIPS	MF	[24]

Membrane processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF)

Methods: temperature induced phase separation (TIPS); non-solvent induced phase separation (NIPS); interfacial polymerization (IP); vapor induced phase separation (VIPS)

Polymers: poly(vinylidene fluoride) (PVDF), cellulose acetate (CA), cellulose diacetate (CDA), poly(lactic acid) PLA, polysulfone (PSU), poly(ether sulfone)(PES), poly(amide imide) (PAI), sulfonated polystyrene (PSS), poly(sodium 4-styrenesulfonate) (PSS), poly(allylamine hydrochloride) (PAH), poly(diallyldimethylammonium chloride) (PDADMAC), and poly(N-ethyl-4-vinylpyridinium) (QVP-C2)

Table 2. “Greener” synthetic organic solvents for membrane manufacture.

Solvent	Polymer	Method	Process	Ref.
Non-ionic solvents				
Dimethyl sulfoxide (DMSO)	PVDF	VIPS	MF	[26]
DMSO EVOL	PES	NIPS/VIPS	MF	[27]
Rhodiasolv® PolarClean	PES	NIPS	MF	[28]
	PES, PSU, CA	NIPS	NF/UF	[29]
	PVC-g-PEGMA	NIPS	UF	[30]
	PVDF/PSU	NIPS	UF/MF	[31]
Butyl Acetate	LDPE	TIPS	UF/MF	[32]
Organic Carbonates	Various	NIPS	NF	[33]
Dimethyl Carbonate (DMC)	Bamboo fiber, PLA	Solvent evaporation	Non-woven	[34]
Ionic liquids				
[BMIM]Tf2N	PA	IP	NF	[35]
[EMIM]OAc	Cellulose	NIPS/dip-coating	NF/UF	[36-38]
	Chitin/cellulose	NIPS Electrospinning	Not tested	[39] [40]
	PMIA/PEI	NIPS/crosslinking	NF	[41]
[EMIM]DEP	Cellulose	NIPS	NF/UF	[38]
	PES	NIPS	NF/UF	[42]
	Polytriazole	NIPS	NF/UF	[43]
[EMIM]SCN, [BMIM]SCN	EXTEM	NIPS	UF	[44]
[EMIM]Tf2N	Poly(ionic liquid)/zeolite	Casting and cross-linking	GS	[45]

Polymers: poly(lactic acid) PLA, poly(ethylene imine) (PEI), poly(vinyl chloride)-g-poly(ethylene glycol methacrylate) (PVC-g-PEGMA), poly(m-phenylene isophthalamide) (PMIA), poly(ether imide sulfone) (EXTEM)

Ionic liquids: 1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide ([BMIM]Tf2N), 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc), 1-3-dimethylimidazolium dimethylphosphate ([MMIM]DMP), 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM]DEP), 1-ethyl-3-methylimidazolium thiocyanate ([EMIM]SCN), 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN)

Membrane production using bio-sourced solvents

Water is not a universal solvent for all membrane-relevant polymers. The next green alternative is the use of bio-sourced solvents. The membrane fabrication by NIPs using various bio-sourced solvents have been demonstrated by different groups (Table 1). Figoli's group has been proposing different solvents, like CyreneTM [19] and isosorbide [20]. Other bio-sourced solvents are methyl lactate [15], γ -valerolactone [17-18], N,N-dimethyl lactamide [21], succindiamide [22], glycerol derivatives [23], 2-methyl tetrahydrofuran (2-MeTHF). [15] Glycerol derivatives such as monoacetin, diacetin, triacetin, glycerol- formal together with 2-MeTHF as a co-solvent can be used for NF membrane fabrication. Rasool et al. [23] analyzed thermodynamic and kinetic aspects, depending on the combination of glycerol derivatives and 2-MeTHF and the

concentration of CA, and examined the resultant morphology of membranes.

Bio-sourced solvents have been also used for membrane production in combination with other methods, e.g. dimethyl isosorbide (DMI), combining VIPS and NIPS [24]. Decanoic acid has been introduced instead of other organic solvents for interfacial polymerization [16].

Membrane production using DMSO

Table 2 lists recent reports on membrane manufacture using synthesized organic solvents with low toxicity. The closest substitute for DMF, NMP and DMAc in terms of polarity and capability of dissolving similar polymers is DMSO. The primary source for DMSO is renewable. DMSO is derived from the wood pulp industry, produced by the oxidation of dimethyl sulfide. It is considered a non-toxic chemical, although some reasons for concern have been recently identified of *in vitro*. [25] The strong characteristic smell is a clear disadvantage. DMSO EVOL™ is a new grade engineered to change the characteristic smell to a much more pleasant one. Procedures for preparation of polyethersulfone (PES) and poly(vinylidene fluoride) (PVDF) membranes using DMSO as solvent have been published by Figoli's and Ulbricht's groups.[26,27]

Membrane production using non-ionic synthetic organic solvents

Among the emerging solvents for membrane fabrication, Rhodiasolv® PolarClean has now been explored by different researchers with increasing interest, applied to a variety of polymers, such as PVDF, polysulfone (PSU), polyethersulfone (PES) and others, as shown in Table 2. This is a polar aprotic solvent constituted by methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate and its diamide derivative in a 20:1 ratio. It is considered non-toxic and therefore has great chances of being even more applied in the industry. The whole production life cycle still has to be fully considered. Particularly interesting is a recent morphology reported for membranes prepared by blending PVDF and PSU in a PolarClean solution. [32] Dimethyl carbonate and other organic carbonates are also quite versatile and an excellent alternative for dissolving polymers of normal interest for membrane manufacture as pure solvent or in combination with others [34]. Butyl acetate is found in fruits, but is also chemically synthesized. It has been recently demonstrated as alternative to much more toxic xylene to dissolve polyethylene in the thermal induced phase separation (TIPS) membrane manufacture. [32]

Membrane production using ionic liquids

Ionic liquids (ILs) consist of cations and anions. Due to the low lattice energy between cations and anions, they exist as liquid. Since they do not have a measurable vapor pressure, the level of produced toxic volatile organic compounds (VOCs) is almost zero. From this point of view, ILs are considered green solvents, although we cannot deny the existence of some controversy in terms of not completely investigated toxicity in water or the sustainability of their production life cycle assessment (LCA). [46] There is a broad variety of ionic liquids and this increases the chances of identifying suitable matches for different polymers, as well as choosing those with highest levels of sustainability. Independent of the environmental aspect, ILs are particularly attractive, because they have the advantage of dissolving materials that have been hardly soluble in other solvents and have led to different morphologies and performance than achieved with other solvents. The best example is the capability of ILs to dissolve cellulose, which has been now explored by different research groups. [36-38] In the last years, the use of ILs has been extended to substitute polar organic solvents, such as DMF, DMAc, NMP, for the preparation of asymmetric porous membranes based in several polymers, by the NIPS method (Table 2).

Besides the application in NIPS, the Vankelecom's group [35] introduced ILs ([BMIM]Tf₂N) as solvent for the organic phase in the preparation of a membrane selective layer by interfacial polymerization.

Furthermore, ILs have been long used as immobilized solvents within the porous support for supported ILs membranes for gas separation. Recently, the Noble's and Gin's groups [45] reported mixed matrix membranes (MMMs) for CO₂/CH₄ separation, prepared from poly(ionic liquid)/IL/zeolite. Dispersed solutions of a curable IL prepolymer and zeolite in [EMIM]Tf₂N were cast on a UF support membrane and then photo-crosslinked to form the membrane.

Membrane production using deep eutectic solvents

Deep eutectic solvents (DESs) consist of hydrogen bond acceptors (HBA) and donors (HBD) and many are of natural source. [47] In membrane production, they are mainly used as immobilized solvents within the pores of preformed supports [48], for surface cleaning and modification of thin film composite (TFC) polyamide RO membranes [49], for the pretreatment of raw materials like silkworm fibers [50] and lignocellulosic biomass [51] to loosen and swell

the structure of materials. DESs were also used as co-solvents or as additives mixed with DMF, NMP, DMAc for porous membrane fabrication.

Outlook

The main driving force for the transition into a more sustainable membrane production using green solvents is the concern on the health of the manufacturing staff and the risk of emissions to the environment. But the final move for implementation will be the establishment of environmental legislation in different countries. Until then, effective alternatives for the currently used solvents and processes have to be proposed and demonstrated. The main considerations are summarized in Figure 3. For membranes to continue to be a sustainable solution for separations, their performance and stability are still priorities in pore ranges varying from RO, NF to UF and MF. In many membrane applications, large areas are required and continuous manufacturing processes are necessary. The manufacturing methods available without solvents, such as lithography and 3D-printing can be successful for selected applications, but are far to provide the needed broad and large scale to cover the whole membrane technology spectrum. Therefore, solvent processes will continue to predominate. Production processes with green solvents should be optimized and ready. Good options have been already reported, each with advantages and drawbacks. For a solution process, the solubilization strength of the solvents and the extension of their applicability are essential aspects. The green manufacture will probably consist of a combination of solutions for selected classes of membranes. Water, is an attractive solution, but can serve as solvent for a limited class of materials. Bio-sourced solvents are advantageous as real green chemicals, with low or no toxicity, high biodegradability, but their success depends on their availability in large scale at accessible costs. Synthetic solvents with solvent strength closer to DMF and DMAc are those with more immediate consideration. Under this category are DMSO, PolarClean and ionic liquids, providing low toxicity to the operators during the manufacturing process and low environmental emissions. Nevertheless, for the holistic sustainability, the life cycle assessment of these solvents is also relevant, as well as the possibilities of recycling to secure zero-discharge.

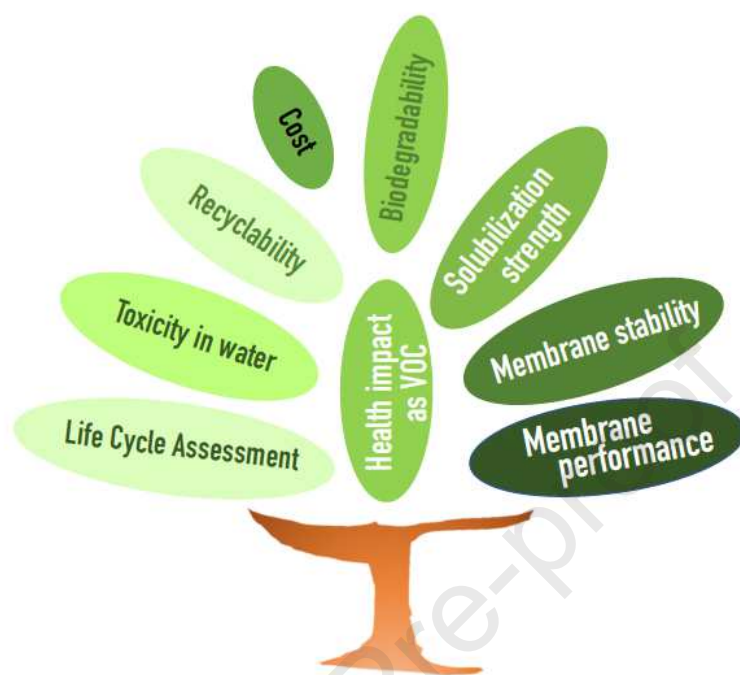


Figure 3. Relevant aspects for green solvent selection and implementation.

Conflict of interest statement

Nothing declared.

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Declaration of Interest Statement

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The authors declare no conflict of interest

A handwritten signature in blue ink that reads "S. P. Nunes".

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