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Toward greener membranes with 3D printing technology

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Abstract

3D printing has recently influenced membrane science. As a green alternative to current membrane fabrication methods, 3D printing prevents the mixing of highly toxic chemicals into water through its sustainable production. Furthermore, the risk of exposure to these toxic materials and of mechanical accidents during the fabrication is also attenuated. This type of in-situ fabrication eliminates logistic-based problems caused by transportation and packaging. Eliminating packaging and reducing transportation and precision-based waste also reduces CO_2 emissions. The advantages of 3D-printed membranes are correlated with each other and promote a greener environment. In this article, we collect their contributions under the sub-titles of sustainability, risk reduction, cost-effectiveness, precision and mobility.

Keywords: 3D printed membranes, Cost-effectiveness, Mobility, Precision, Risk reduction, Sustainability

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1. Introduction

As the water-energy nexus has become the primary concern related to the outcomes of global warming, a need for energy-efficient methods for water purification has emerged [1-3]. Membrane technologies have already been widely adopted for real-life applications. However, compared to other purification methods, membrane treatments have crucial drawbacks that must be solved. Fabrication techniques are important in addressing these drawbacks.

Over the last few decades, phase inversion, interfacial polymerization, stretching, track-etching and electrospinning have been the most widely used conventional techniques. Phase inversion was introduced in 1960 and is the current basis for most commercially available membranes [4, 5]. Most porous polymeric membranes are fabricated via non-solvent induced phase separation (NIPS) and thermally induced phase separation (TIPS) methods [6]. For NIPS, the polymer solution is immersed in a non-solvent coagulation bath resulting in the exchange of solvent and non-solvent to form an asymmetric, dense surfaced membrane that can be used for reverse osmosis (RO) and nanofiltration (NF) systems. Demixing and precipitation occur during the NIPS type fabrications. TIPS is applied with semi-crystalline polymers and utilizes the thermal energy of a dope solution as the main driving force. They provide highly porous symmetric structures, which are suitable for microfiltration (MF) and membrane contactor applications [7-9]. It is based on the decrease in solvent quality as a result of decreased temperature. After the demixing, the solvent is removed by extraction, evaporation or freeze drying [10]. The main problem of these methods is the waste of huge amounts of solvents. Furthermore, with these methods, it is difficult to control the precision and the uniformity. One of the most promising methods for the future of membrane fabrication is interfacial polymerization. Conventional interfacial polymerization has been conducted by immersing the support into monomer solutions followed by heat treatment.

Although this method has the same waste and uniformity problems as NIPS and TIPS, it has recently been developed further through the use of 3D printing.

In 2018, Ma et al. [11] introduced the first 3D printing–assisted thin film composite (TFC) membrane fabrication by electro-spraying two monomer solutions to fabricate a polyamide layer through interfacial polymerization on a polymer substrate. This approach was further developed to fabricate the first self-standing 3D-printed ultrafiltration (UF) membrane [12]. Rather than getting the advantages of interfacial polymerization such as high perm-selectivity properties, electro-spraying based these works are also the initials of future 3D-printed membranes, which can utilize further approaches that can even design the pore structures through computer modeling. In addition, 3D printing offers more in terms of sustainability, risk reduction, cost-effectiveness, precision and mobility (Fig. 1). Here, we present these major points that designate 3D printing as a promising, green revolution for the fabrication of polymeric membranes.

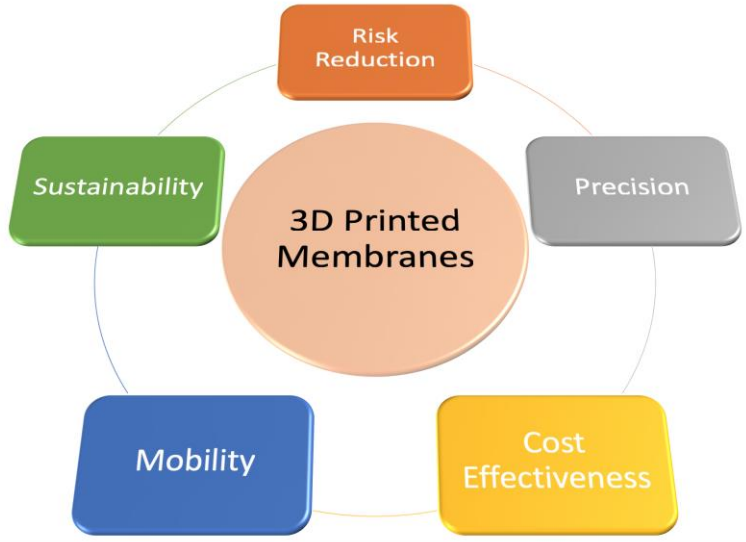

Fig. 1. Five breakthroughs that 3D printing offers for membrane fabrication.

2. Five Breakthroughs of 3D Printed Membranes

2.1. Sustainability

Manufacturing is responsible for 33% of the total carbon footprint [13]. This ratio will increase as the energy required for manufacturing increases. According to the International Energy Outlook 2017, prepared by U.S. Energy Information Administration, energy consumption by manufacturing will increase steeply by 2040 [14] (Fig. 2). However, some recent projections show that these consumptions could be reduced substantially by 3D printing. As a derivation of 18 projections, Delphi projections show that the carbon footprint of manufacturing and transportation will be greatly reduced by 3D printing [15]. When considering membrane fabrications, these ratios increase.

Although membrane processes are known as green processes, the same cannot be said about fabrication. Membrane fabrication requires highly toxic and dipolar aprotic solvents like N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAc) [16, 17]. Fifty billion liters of solvent-containing wastewater are generated every year when these solvents are mixed with water during the membrane fabrication [18] (Fig. 3). Further disposal of these solvent results in a huge amount of CO_2 emissions. For example, the fabrication of TFC membranes with phase inversion methods creates a large amount of liquid and gas waste during solution casting, phase inversion (very high), solvent swapping, crosslinking, washing, conditioning, coating and active layer formation processes. Different from the conventional methods, 3D printing does not use membrane materials more than required amount, and it also eliminates coagulation bath. Therefore, the huge amount of wastes production highly decreases, so does resulting CO_2 emissions.

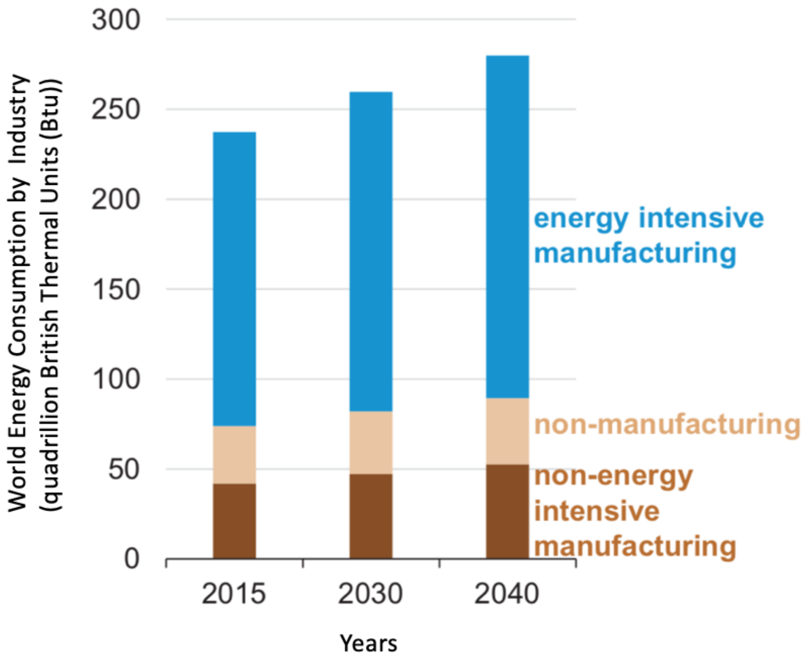

Fig. 2. Effect of manufacturing on energy consumption. The image is reproduced from a previous study [14] of U.S. Energy Information Administration.

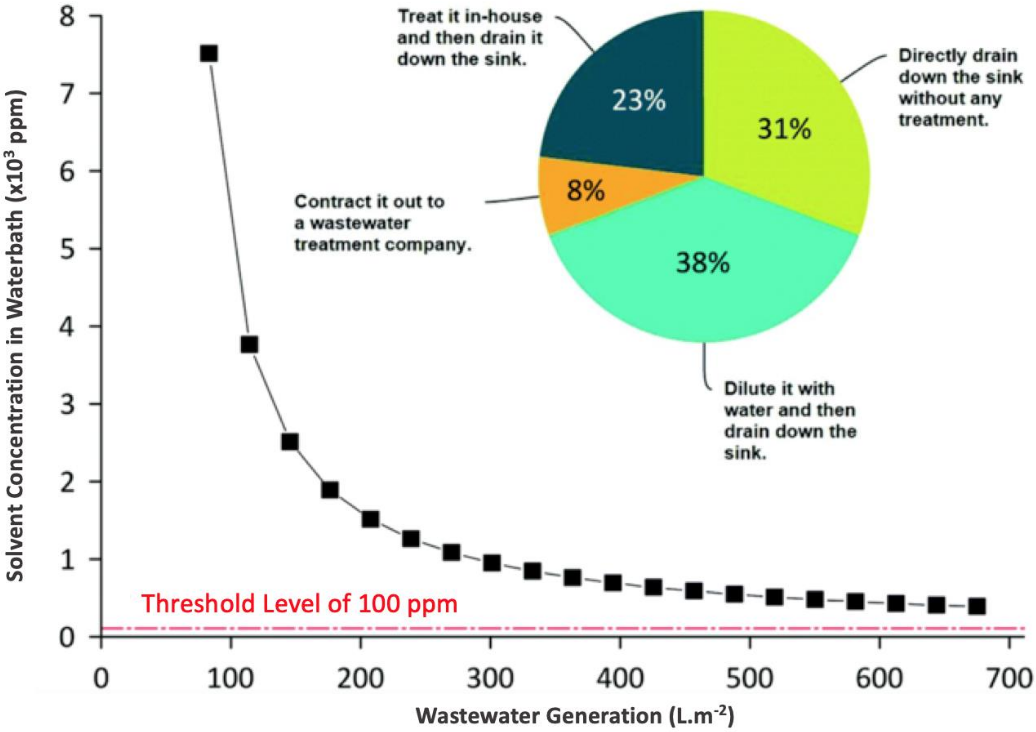

Fig. 3. Calculated solvent concentration in the wastewater during conventional membrane fabrication processes with the threshold level for requiring an appropriate treatment prior to disposal or reuse. This figure shows the outcome of a survey conducted by Razali et al. about

how membrane manufacturing companies dispose of coagulation bath wastewater. The image is reproduced from Ref. [18] – Published by The Royal Society of Chemistry.

2.2. Risk Reduction

Synthesis of a polymeric membrane requires toxic materials, exposure to which can pose a health risk. Even when precautions are taken, there are still risks of harm by those materials. Current phase separation processes for membrane fabrications require a homogeneous polymer solution to transform into a two-phase system. The solid, polymer-rich phase forms the membrane structure, while a liquid polymer-poor phase forms the porous structure [19]. During the process, the polymer is dissolved in a mixture of a volatile good solvent and an involatile poor solvent. This is followed by the evaporation of the good solvent, which enriches the cast film in non-solvent, causing precipitation. The preparation process of the solvent and the evaporation of the volatile solvent creates a high risk of exposure. Exposure to these toxic solvents can result in various health problems, ranging from light skin problems, headaches or irritation to life-threatening illnesses including cancer and permanent neural problems (Table 1). Detailed risks of these solvents are provided in Table 1 together with the most common solvents.

Through 3D printing–based membrane fabrications, the risk of exposure will be reduced to a minimum level as 3D printing is a process which is controlled by remote commands through a computer.

When industrial fabrications are considered, there is an additional risk of accidents occurring during the mechanical processes. Such accidents will also be reduced to some extent with the assistance of 3D printing. In addition, because of the in-situ nature of 3D-printing fabrication, transportation accidents will be eliminated.

Table 1. Toxic solvents used during membrane fabrication and their related health effects (* indicates results obtained from animal experiments).

Solvent for Membrane Fabrication	Negative Health Effects
Acetone	Short term: heavy, vague, or faint feeling in the head; nausea; loss of weight; and slow healing of an external wound. Long term: irritation, tearing, and acetone odor [20]
Benzene	Acute leukemia and likely other hematological cancers [21]
n-butanol	Eye redness, lipid layer thickness, and bronchial responsiveness [22]
Cyclohexane	Diverse effects on body weight, clinical chemistry, tissue morphology, and neurobehavioral parameters [23]*
1,2-dichloroethane (1,2-DCE)	Alteration in adrenal gland, kidney, and liver weights, and morphologic alterations in the kidney and liver [24]*
N, N-dimethylacetamide (DMAc)	DMA can stick to the skin, [25] cardiovascular malformations, ultimate problems for maternal bodies [26]*
Dimethylformamide (DMF)	Dose-dependent increase in subjective symptoms, digestive system-related symptoms such as nausea and abdominal pain, prevalence of alcohol intolerance [27], toxic influence of DMF on liver function and liver enzyme abnormalities [27-30]
Dimethyl sulfoxide (DMSO)	Rash, abdominal cramps, back/bone pain, dysgeusia, dyspnea/cough, macrohematuria/proteinuria and cardiovascular problems [31]
Diethyl ether	Stimulation of stress hormones, behavioral and neuroendocrine activating effects* [32]
Heptane	Damage to peripheral nerve* [33] and urinal problems [34]
Hexane	Outbreaks of peripheral neuropathies [35-38]
Methanol	Retinal dysfunction* [39]
Methyl-t-butyl ether (MTBE)	Headache; nasal, throat, or ocular irritation; nausea and vomiting; dizziness; and sensations of "spaciness" and disorientation [40]
Methyl ethyl ketone (MEK)	Peripheral nerve changes (axonal swelling or myelin thinning, inpouchings of the myelin sheath, abnormalities at the neuromuscular junction) [41]
N-methyl- 2-pyrrolidone (NMP)	Focal pneumonia, bone marrow hypoplasia, and atrophy of lymphoid tissue in the spleen and thymus,*[42] irritation of the eyes, the upper respiratory tract and headaches [43]
n-propanol	Skin irritation [44]
Isopropanol	Peripheral nerve toxicity [45]

Tetrahydrofuran	Increased succinate dehydrogenase activity, and muscle acetylcholine esterase activity [46]
Toluene	Auditory nervous system problems [47] and problems in spatial learning and memory [48]
Xylene	Various effects on many organ systems, including the CNS, liver, kidney, hemopoietic tissues and respiratory tract [49]

2.3. Cost-Effectiveness

Since its inception, 3D printing has become integrated into almost every area of science; one of the main reason for this is the reduced fabrication cost that is associated with 3D printing. However, when we consider membrane science, the situation is more relative to the scale. Considering the current situation of 3D-printing technology, it would be controversial to say low-cost fabrication when it comes to the ones requiring nano-precision. Long printing times and complex machinery make even sub-micron pored membrane fabrication very costly [50]. However, the research of Chowdhury et al. [12] demonstrates the promising future of low-cost 3D-printed membranes.

The main cost advantage of 3D printing for membrane fabrication is the ability to fabricate required amount without wasting materials. Unlike the materials wasted during the phase inversion of conventional fabrication methods, 3D printing does not use more materials than required. Comparing immersing type and electro-spraying type interfacial polymerizations clearly demonstrates this difference. Another important benefit of 3D printing is the reduction in labor cost for mass production. Machines will eventually replace some human laborers through the application of 3D printing. When in-situ fabrication of membranes become common, shipping and packing costs will also no longer be a concern [51]. In addition, bespoke fabrication for the membrane sizes required for specific needs will reduce the cost associated with sizing the membrane.

2.4. Precision

3D printing is a precise fabrication method that produces complex structures in macroscale [52, 53]. Although was previously unheard of to say the same thing about micro and nanoscales, recent developments in 2-photon polymerization by spatiotemporal focusing of the femtosecond laser pulses made it possible to have ≈100 nm resolution [54]. It is currently possible to do surface printing around 60 nm resolution through super-resolution laser direct writing [55]. This can go down up to 20 nm when lithographic methods are considered, which was previously applied successfully at Caltech in the creation of nano-architected metals [56]. It is not a huge leap to go below 10 nm resolution, which will allow us to adjust the pore sizes of the polymeric membranes more precisely.

The developed precision of 3D printing will also let researches apply biomimetic structures successfully. Indeed, it has been successfully applied in micro-scale by mimicking surfaces from nature. Immersed surface accumulation 3D printing of micro-scale artificial hairs with eggbeater heads, which mimic the Salvinia molesta leaf, is an example of this [57]. As 3D-printing technology is further developed, we will likely see this research approach in nano-scale as well.

Furthermore, precise fabrication also provides uniformity for 3D-printed membranes. Current fabrication methods cannot produce uniform membranes with uniform pore distribution and thickness. The size control properties of 3D printing would bring uniformity to this area of membrane science, helping to clear away any possible conflict between producers and customers.

2.5. Mobility

3D printing is a convenient fabrication method that is versatile, rapid and in-situ (making it ready to use for any case in place). Furthermore, it is possible to fabricate complex structures to order without having to account for transportation time. In this way, on-demand fabrication carries great importance. One 3D printer launched by the National Aeronautics and Space Administration (NASA) at the International Space Station in 2014 is an example of the mobility of additive manufacturing technologies. With this 3D printer, astronauts are able to produce various types of objects according to their requirements, such as replacements for broken parts or innovative tools under space conditions [58].

The mobility of 3D printing applies to membrane science in several ways. In-situ fabrication of membranes is highly beneficial for desalination membranes in particular as these types of membranes are mostly required in dry regions as in Gulf countries. The high temperature in such arid areas can result in the loss of membrane properties. Therefore, high-cost protections are needed until the membrane starts its filtration life. In-situ fabrication will reduce the length of the waiting period before use. Furthermore, in the case of urgent requirement, any broken or damaged module part of a membrane system can also be rapidly produced and replaced through 3D printing. This type of fabrication can also be incorporated with 3D scanning.

3. Current State and Limitations of 3D Printed Membranes

Most of the limitations for 3D printed membranes come from the current status of 3D printing technology. 3D printing technology has already reached nano-scale production level. However, for this level, the precision that we mentioned in previous paragraphs becomes a critical problem. Even though, 3D printing is advantageous for the precision of micro or macro level fabrications, further developments are required for the nano-scale. Nevertheless, this applies to current fabrication methods as well, since they are not precise in nano-level [59]. Therefore, as the technology develops, 3D printing is expected to be the leading technology for nano-scale fabrication.

Huge sizes of 3D printers are another barrier to the current 3D printing technology in terms of footprint. Even for the fabrication of small sized objects, massive 3D printers are required. Consequently, mass production of the products becomes difficult as well.

Another issue that serves as a limitation to the use of 3D printers is price. Even though the machine printing in macroscales is affordable, micro or nano-scale printing ones are difficult to afford to the most regions of the world [60]. The high prices are also related to large sizes of current printers. That is, when printing scale is reduced to micro and nano-sizes, more complex machines with larger sizes are required. The greater material and assembly costs of these machines result in the higher prices.

Lastly, most of the 3D printers, especially the ultra-precise ones, are not able to fabricate with common materials used in simple 3D printers. They are designated to print with specific materials, such as Accura, Duraform, FabPro or Visijet series: polypropylene-like printing materials of 3D Systems [61].

These limitations of 3D printing technology are eliminated day by day as result of on-going researches. Therefore, it is not very far to see convenient size and ultra-precise 3D printers that is able to print with any selected material.

4. Conclusions

As a greener alternative to current high-waste membrane fabrication methods, 3D printing minimizes the waste created during the production, packaging and transportation processes. Furthermore, the risks are also reduced by remote fabrication.

Currently, research related to 3D-printed membranes is still in its infancy. However, as 3D printing itself continues to develop, membrane fabrication utilizing the technology will also develop and will be commonly applied in water treatment and desalination plants. Researchers should pay further attention to 3D-printed membranes by considering their major contributions as a sustainable, risk-reducing, cost-effective, precise and mobile fabrication method for a greener environment.

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Author Contributions

This work has been held under the coordination and supervision of H.C.(Professor). N.Y.(Ph.D student) has done the scientific literature review and written the manuscript by also preparing the figures as first author. M.S.(Postdoctoral fellow) and H.P.(Research Professor) have revised the manuscript for several times and added critical parts to the manuscript for the final version.

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