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Review

A New era of water treatment technologies: 3D printing for membranes

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A B S T R A C T

The commercialization of sustainable 3D printing technology changed the face of manufacturing with its precise and uniform sustainable fabrication. Therefore, like other fields of science, research related to water treatment membranes has adopted this technology successfully, preventing the waste of huge amounts of solvents and thus reducing the high carbon emissions caused by fabrication. Currently, critical research is being conducted in relation to the membrane modules and the fabrication of the membranes themselves. The module studies focus primarily on spacer production and the membrane studies are mostly concerned with the membrane surface. The membrane surface research has successfully adapted inkjet printing for enhanced surface properties for high selectivity and fouling resistance through the printing of nano-materials on the membranes' surfaces. Recently, 3D printing of the polymer membrane support or 3D printing-based interfacial polymerization has also been introduced into water treatment technologies. Since fouling resistance, selectivity and water permeability are the critical factors, many of the parameters can be controlled by the assistance of bespoke and precise 3D printing fabrication. In this study, we examine key aspects of technology which may shed light on future studies regarding 3D printed water treatment membranes and we review the critical developments to date.

Contents

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Introduction

History of 3D printing

Fabrication is the main process for manufacturing the various tools and equipment that we use daily. Until 1980, traditional manufacturing methods were employed to produce the many different types of tools. However, in the early 1980s, the introduction of a new manufacturing method, named 3D printing, applied materials layer by layer, boosting the development of both manufacturing and its associated technology. The early version of 3D printing used a laser to fuse a layer of powdered material, leading to the basic version of Fused Deposition Modelling (FDM) printers [1]. The technology was further improved when Alain Le Méhauté, Olivier de Witte, and Jean Claude André invented stereolithography (SLA). SLA is a vat printing technique based on photopolymerization of liquid polymers by ultraviolet (UV) light to turn into solids [2]. Later on, Chuck Hull patented new 3D systems technology using stereolithography files [3,4]. Finally, modern manufacturing was ushered in by the production of the first 3D printer, also developed by Chuck Hull, which was patented as “Apparatus for the Production of Three-Dimensional Objects by Stereolithography” [5].

Standard triangle language (STL) and computer aided design (CAD)

Standard Triangle Language (STL) files are the main bridge for converting geometric design into a header, small triangles, or an x, y, and z coordinate list, and normal vectors [6]. These geometries are modeled by Computer Aided Design (CAD) software before the STL files are prepared for the bespoke fabrication [7]. (Fig. 1). CAD modelling allows users to design structures ranging from very simple to highly complex [8,9]. After the STL file is created by the CAD software, slicing takes place. Slicing software is used to prepare a file containing cross-sectional layers of the model and send this file to a 3D printing machine [10]. In addition to CAD-based model preparation, 3D scanning is another method for the replicative printing of already existing objects [11,12]. This method is important for the fast production of urgently needed replacement machine parts or devices.

Classification of 3D printing methods

Today, manufacturing utilizes various types of 3D printing methods that can be assigned to three main categories: liquid-based, solid-based and powder-based [14–17]. Although they are classified according to the type of printing material they use, they can also be classified according to the procedures of photo-curing, cutting and joining, melting and solidifying, and joining/binding [18–20]. Since the invention of Stereolithography Apparatus (SLA) for 3D systems, various novel systems have utilized these 3D printing methods (Table 1) [21]. Comparatively recent inventions such as two or multi photon polymerization (2 P P or MPP), which employ nonlinear photon absorption by photopolymers [22–24], have yet to be classified. These 2 P P and MPP systems work with the absorption of two or more photons and local polymerization [25]. Furthermore, according to American Society for Testing and Materials (ASTM), 3D printing can be classified into seven categories: (1) binder jetting; (2) directed energy deposition; (3) material extrusion; (4) material jetting; (5) powder bed fusion; (6) sheet lamination; and (7) vat photopolymerization [26,27].

Role of 3D printing for water treatment membranes

As 3D printing’s itself gets developed, other areas of science also get an acceleration from that. Sustainability, uniformity, precision, bespoke fabrication of laboratory or pilot scale samples, and the rapid fabrication of the replacement parts are the main advantages of additive manufacturing for scientific applications. Currently, various fields of science, from mechanical engineering to chemistry or even biology, have benefited from the increasing number of research studies dealing with the development of 3D printing [28,29]. Recently, environmental science and engineering also started to benefit from 3D printing [30]. In particular, the fabrication of miniaturized devices for toxicity management and environmental assessments, and some specific parts of water treatment systems or membrane modules, are beginning to utilize this technology [31]. Although the application of this technology to water treatment systems started with membrane module studies, the fabrication of membranes themselves is a new field of research. Our study therefore examines how 3D printing can be utilized for the manufacture of water treatment membranes.

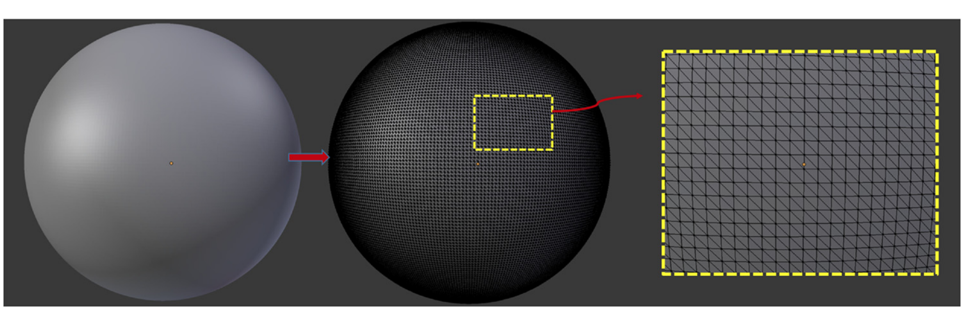

Fig. 1. Graphic representation of the spatial coordinates of the triangle vertices stored in the STL file before transmission to the printer for fabrication. The image (inspired by a previous study [13]) was drawn by our group using Blender modelling software.

Table 1
3D printing methods based on different types of printing materials.

Type of material used	Type of the printing system	Specific feature of the application
Liquid based	Stereolithography Apparatus (SLA)	Single laser beam method
	Solid Object Ultraviolet-Laser Printer (SOUP)	
	Multijet (MJP) Printing	UV curing
	Polyjet	
	Prefactory	Digital Light Processing (DLP)
	Bioprinting	Extrusion in liquid medium
	3D Bioplotter	
	Rapid Freeze Prototyping	Freezing and deposition of water droplets
Solid Based	Fused Depositiopn Modelling (FDM)	Melting and solidifying/Fusing
	Benchtop System	
	Selective Deposition Lamination (SDL)	Cutting and joining
	Laminated Object Manufacturing (LOM)	
	Ultrasonic Consolidation	
Powder Based	Selective Laser Sintering (SLS)	Joining and binding
	• Colorjet Printing (CJP)	
	• Laser Engineered Net Shaping (LENS)	
	• Electron Beam Melting (EBM)	

As the effects of global warming have become an increasing threat to humanity, the need for potable water has increased dramatically [32–34]. As a result, water treatment and desalination technologies have become increasingly important for the recycling and reuse of available but undrinkable water supplies [35]. Hence, membrane science and technology have also become crucially important because their high removal capacity and energy efficiency provide a potential solution for the water scarcity problem [36–40]. The urgent requirement for high-efficiency membranes also necessitated quick and precise fabrication and the application of 3D printing was therefore adopted by researchers.

Precise fabrication of water treatment membrane is further important for water-energy nexus. Having robust and ultra-thin membranes with uniform pore sizes would further be possible through 3D printing. Layer by layer nanoscale-printing of membranes would allow well -arranged pore size with robust structure. Through 3D printing, perm-selectivity of water treatment membranes would also be possible controlled.

In addition to precise or quick fabrication, economic and less wasteful production makes the use of 3D printing important for membrane fabrication. Non-solvent induced phase separation (NIPS), thermally induced phase separation (TIPS), and vapor induced separation have been the most common membrane fabrication methods [41–43]. However, these methods require a large amount of solvent, which produces large quantities of harmful waste and leads to environmental pollution [42]. Monomers for membrane fabrications such as N-methyl-2-pyrrolidone (NMP), N, N-dimethylformamide (DMF) or N,N-dimethylacetamide (DMAc) are highly toxic materials that can also have significant negative effects on human health [44–48]. Furthermore, 50 billion liters of waste water per year is generated as a result of mixing of these toxic materials with water during the membrane fabrication process [49]. When we consider the emissions generated during the treatment of 50 billion liters of waste water, the transportation of the fabricated membranes and the isolation packs for them, the carbon footprint becomes a further concern. In addition, the non-uniform fabrication associated with these conventional methods results in high amounts of waste [50]. Consequently, 3D printing, with its low-waste fabrication method and low chemical exposure process, has great importance for green environments [51].

Table 2
3D printing for water treatment membranes with corresponding precision, and printing material.

	3D Printing Type	Current Achievable Precision: XY/Z	Printing Material	Membrane Application
3D Printing	Fused Deposition Modelling, [53] [54],	12.5 um/10 um (78.25 um step size)	Thermoplastic Polymeric Filaments	Module applications, support layers or sacrificial support layers, oil water separation membranes
	Stereolithography Apparatus [53–56]	20 um/10 um	Photopolymer Resin	Module applications, support layers or sacrificial support layers, oil water separation membranes
	Digital Light Processing [54,56]	29 um/35 um	Photopolymer resin	Module applications, support layers or sacrificial support layers, oil water separation membranes
	Polyjet, [54,57]	600 × 600 × 907 dpi / 16 um	Photopolymer resin	Module applications, support layers or sacrificial support layers, oil water separation membranes
	Multijet [57]	750 × 750 × 890 dpi /29 um	Photopolymer resin	Module applications, support layers or sacrificial support layers, oil water separation membranes
	Selective Laser Sintering [54,58]	50 um/50 um	Thermoplastic polymeric powder	Module applications, support layers or sacrificial support layers, oil water separation membranes
	2 P P Two Photon Polymerization [59]	0.036 um	Liquid photopolymer	Microfiltration, Ultrafiltration
3D Printing Based	Inkjet Printing [57]	300 um-600 um/15–50 um (20 um droplet size)	No restriction (liquid)	Thin Film fabrication (active layer fabrication) for (Reverse Osmosis / Forward Osmosis Membranes etc.)
	Bioprinting/ 3D Bioplotter [21,60]	>500 um	No restriction (liquid)	Thin Film fabrication (active layer fabrication) for (Reverse Osmosis / Forward Osmosis Membranes etc.)
	Electrospraying based [61]	Uncontrollable/4 nm	No restriction (sprayable solutions)	Self-standing desalination membranes, Thin Film fabrication (active layer fabrication) for (Reverse Osmosis / Forward Osmosis Membranes etc.)

Synopsis: 3D printing carries great importance for the sustainability of future water treatment membranes with its low-waste and low chemical exposure fabrication process.

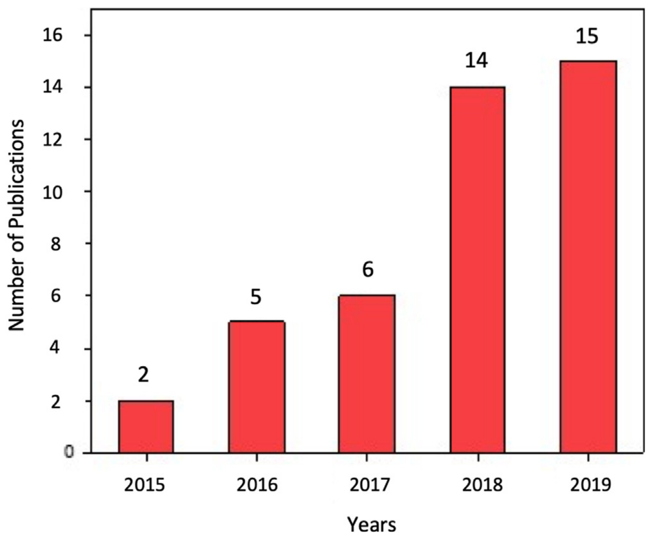

Fig. 2. Number of publications related to 3D printed water treatment membranes (The graph was drawn from Scopus data by our group).

The technology is currently applied to the printing of the membrane module parts and the support layer of the membrane, or as inkjet printing for the membrane surfaces (Table 2). Although research studies are still uncommon, the amount of research and the number of scientific articles is increasing as the 3D printing technology continues to develop (Fig. 2). 3D printing technology has been revolutionizing the designs of membrane modules, and it is expected to reduce the energy consumption and chemical usage in the seawater desalination and waste water treatment plants [52]. Therefore, to accelerate this revolution, it is vital to examine all the key aspects of technology in one article, identifying what has been done so far and what further research is needed.

In this perspective article, we aim to summarize the efforts to apply 3D printing to the manufacture of water treatment membranes, elucidating our perspectives and insights. A couple of published review articles dealt with 3D printing applications for membrane module design, separation membranes and environmental science more generally. However, 3D printing for water treatment membranes requires a specific attention as water-energy nexus has become the most crucial concern of the earth and requirement of the fabrication high efficiency membranes has emerged. Through 3D printing, in-situ fabrication will reduce the cost of both transportation and protection. These two issues are of great importance, especially for desalination plants in countries with ultimate temperature levels. With this article, it is aimed at increasing the attention of scientists and engineers to accelerate development by collecting the crucial researches that have been done so far. This review has its novelty by covering all the crucial aspects of 3D printing applications for water treatment membranes. Differently from the previous review articles on the similar subject, this has a stronger focus on water purification membranes by excluding affiliated researches in other fields, and including all critical up-to-date researches. For a comprehensive explanation, we tried to collate previous researches in two separate areas: the fabrication of module parts and the fabrication of the membranes themselves.

Applications

3D printing applications for the fabrication of membrane module parts

Membrane spacers

Since 3D printing technology is still inconvenient for fabricating membranes, studies began with the application of the technology to membrane module parts. Therefore, major developments focused on module studies [62]. These studies commenced with the production of membrane feed spacers with modified-filament/twisted-plates, multi-layer spacers with twisted tapes, and multi-layer spacers with normal filaments, with a Selective Laser Sintering (SLS) type printer after 3D CAD modelling. This research is important for understanding that Computation Fluid Mechanics (CFD) based filament research can be unreliable because of its intricate geometry, as this research proved by showing that modified filaments and twisted tapes give reduced performance but multi-layer structures may give enhanced performance. This contrasts with the findings of earlier CFD studies [63]. Since those studies, many types of research have focused on new design approaches for membrane feed spacers. Although some research has focused on modifications of commercial diamond design such as changing the angle parameters (Fig. 3a), [64] other research has formulated new shapes or patterns for the spacer fabrication such as for triply periodic minimal surface (TPMS) spacers (Fig. 3b). Among the new shape applications, the TMPS spacer of Sreedhar et al. [65] brought a new approach to spacer applications. By using EOS and the PA 2202 (black) thermoplastic powder as the printing material, SLS printing of spacers was done by the plastic laser sintering system Formiga P 110. As a result, the Schwarz primitive (P-skeletal), the Schoen Gyroid, and the Schwarz crossed layers of parallel (CLP) types of TMPS structures were employed. CLP sheet TPMS (CLP-sh) and the Gyroid and Primitive surfaces (hGyroid-sk and Schwarz P-sk) were further employed to fabricate skeletal TPMS feed spacers through 3D printing. Deviations compared to the design was measured as Schwarz P-sk = 14%, Gyroid-sk = 19%, CLP-sh = 59%. After printing is completed, spacers were tested and topology-induced fouling was reduced with the help of the intertwined geometry, increasing the turbulence of the feed flow. As a result, the increased interaction of the membrane with the flow and enhanced water mixing led to highly increased process performance. It was observed that the water flux was enhanced by as much as 15.5% and 38% for reverse osmosis (RO) of brackish water and ultrafiltration (UF) with sodium alginate solution, respectively. In addition, biofouling of total organic carbon (TOC) was greatly reduced by this new type of spacer. The Gyroid-sk type TMPS spacer reduced the amount of TOC on the membranes' surface by 91% while for the Schwarz P-sk and CLP-sh spacers the amount was 65% and 46% respectively [65]. At the end of the operation, spacers did not show any mechanical deformation; that is, they are suitable for commercial use as well. Pressure drop is also reduced through TPMS spacers. Schwarz P-sk had the best performance with 12.5% less pressure drop than less than that of the commercial spacer. The same research group applied TMPS spacers to the membrane distillation (MD) process and introduced a transverse-CLP spacer which enhanced the flux up to 60% compared to the commercially available net type spacers by also enhancing scaling and organic fouling resistance [66–68]. Another stepping-stone for membrane science is brought by the development of full-contact honeycomb shaped membrane supports (spacers) with the assistance of 3D printing. This type of spacer is the first of its kind as it is specifically developed for FO membranes. The shear distribution provided by the honeycomb structure reduced reverse solute diffusion and surface fouling by up to 50% (Figure 3 g) [69].

Another 3D printed spacer was applied to the manufacture of electro dialysis (ED) membranes. In the study of Bai et al., five types of spacers were fabricated by 3D printing methods in order to improve the limiting current density (LCD), the stack voltage, and the pressure drop of the ED system. Porous spacers were fabricated by a FDM type 3D printer (Replicator 2X, MarkerBot) with acrylonitrile butadiene styrene (ABS) filament with some small defects. The fifth spacer with modified cubic elements showed the highest LCD as 2.0–3.5 times greater than that of the non-spacer

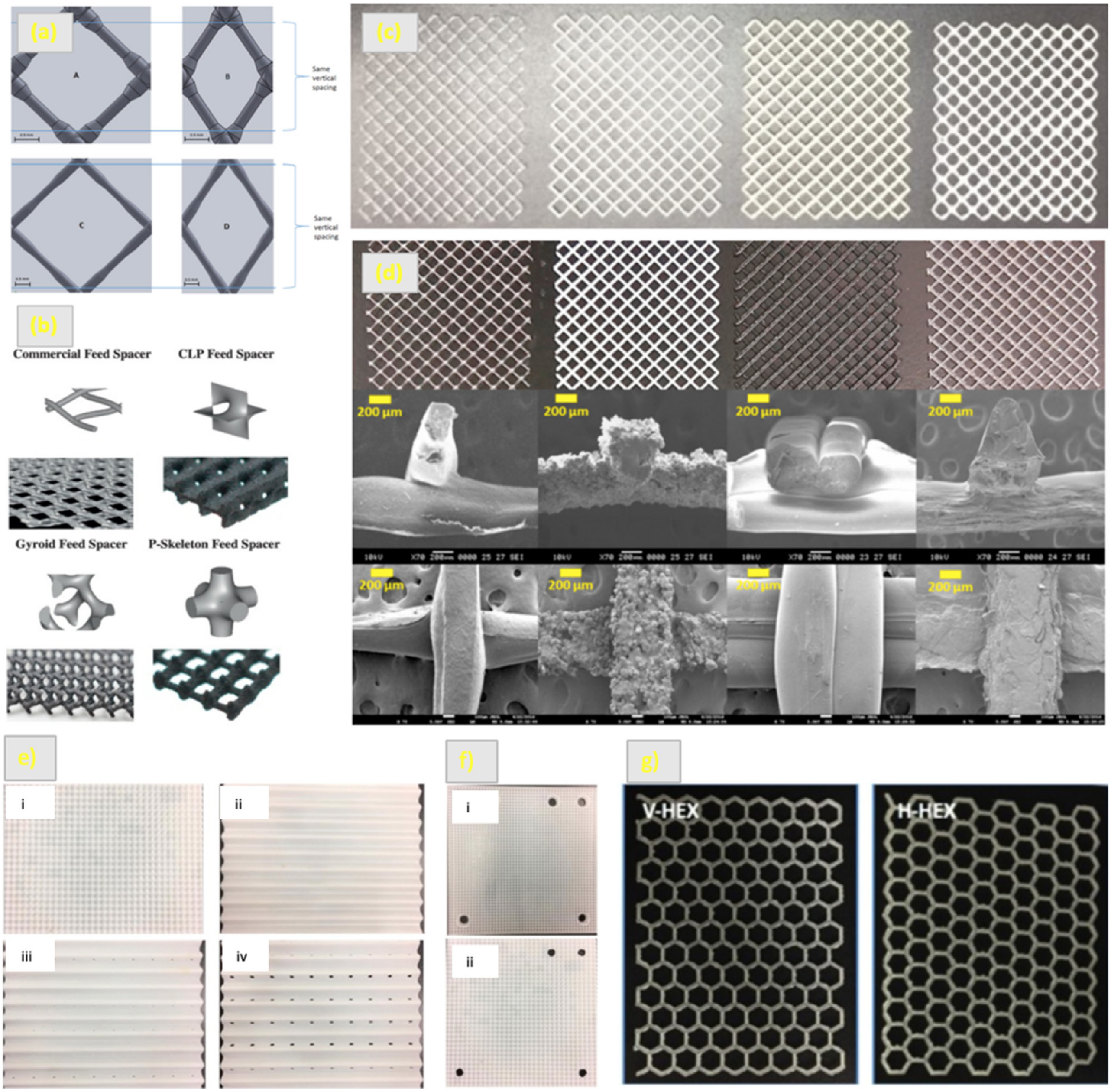

Fig. 3. Spacer studies **a)** Mathematically modeled standard feed spacer, spacer with modified filament angle, spacer with modified mesh size, and spacer with modified filament angle and mesh size (reproduced from a previous study [64] with the permission of Elsevier). **b)** Commercial and TPMS spacers with photos and SEM images (scale bar length is 3 mm) (reproduced from a previous study [65] with the permission of Elsevier). **c)** The Commercial Spacer (Com), PP spacer, ABS spacer, and PLA spacer from left to right, respectively (reproduced from a previous study [71] with the permission of Elsevier). **d)** i) Photo images, and SEM images of the cross section/top view of Commercial (28 mil) spacer, SLS printed spacer, FDM printed spacer, and Polyjet printed spacer respectively (reproduced from a previous study [72] with the permission of Elsevier). **e)** Vibrating spacers i) repeating protrusions like hills and ii, iii, iv) waves (reproduced from a previous study [73] with the permission of Elsevier). **f)** i) 2D vibrating spacer, ii) 3D vibrating spacer, (reproduced from a previous study [74] with the permission of Elsevier). **g)** Honeycombed spacer V-HEX (vertically aligned) and H-HEX (horizontally aligned) (reproduced from a previous study [69] with the permission of Elsevier).

system. It also had a lower electrical resistance and stack voltage. However, pressure drop is also highly enhanced. Especially, spacer 2 is non-usable performance with 5 kPa drop [70].

In addition to the studies regarding the shape of the spacers, some research has focused on the material of the spacer or the 3D printing method's effect. Yanar and Choi et al. [71] compared the effects of using acrylonitrile butadiene styrene (ABS), polypropylene (PP), and polylactic acid (PLA) as printing materials in comparison with a commercially available spacer (Com) and compatible performances were observed in terms fouling, water flux, and mechanical strength (Fig. 3c). To design the 3D spacer model, Autodesk Meshmixer and Blender were utilized. Final products were produced by a PolyJet type 3D printer, used for PP spacer, and a FDM type 3D printer, used for PLA and ABS spacers. Compared to the CAD model with a 20.5 mm^2 open area for each hole; PP, PLA, and ABS and deviations with 20.6 mm^2, 20 mm^2, and 19.8 mm^2 average open areas, respectively. In terms of mechanical strength, the PLA spacer showed the highest yield, with 0.433 MPa, followed by the ABS, Com, and PP spacers, respectively. This research is important for better understanding the spacer and foulant interaction. It was observed that as the foulant interaction with the spacer increased, depending on the spacer material, the high ratio membrane fouling was reduced [71]. It can also be further extended by the printing of other Tan et al.[72] compared liquid, powder, and solid forms of 3D printing for spacer production. In that study, FDM, SLS, and Polyjet type printers were used for solid, powder and liquid forms respectively. Polyamide 12 based white powder material for SLS type, a thermoplastic ABS filament for FDM type, and a photopolymeric liquid material with a support material for Polyjet type 3D printing were utilized for the fabrication. While Polyjet had the best surface finish properties with the least deviation in comparison with CAD model, the spacer printed by the FDM type printer had the highest deviation (Fig. 3d). However, mass transfer of the FDM printed spacer was comparatively the best. In terms of mass transfer and critical flux, the replicated products gave better results than the commercially available product spacer. In terms of mass transfer and critical flux, the replicated products gave better results than the commercially available product spacer. For pressure drop, FDM spacers exhibited the highest power numbers (proportional to pressure drop) than the SLS and Polyjet spacers [72]. 3D printing is also a great assistant for introduction converging technologies. Vibrating spacers are the example of that. Tan et al. [73] (Fig. 3e) and Wu et al. [74] (Fig. 3f) fabricated vibrating spacers by the assistance 3D printing. Enhanced shear rate and turbulence through the new type spacers increased the fouling mitigation for the flat type membranes.

In general, most 3D printed spacer research still cannot go beyond the preliminary level. The applicability of 3D printed spacers for desalination or water treatment plants should be investigated. Therefore, the results of the research should also be supported by pilot applications. In addition, most membrane modules are fabricated as spiral-wound type because of their higher efficiency. However, current spacer studies focus only on flat-type modules. Research on spiral-wound type modules is urgently needed. More critically, mechanical strength studies should be covered with more details. Rather than just tensile strength, bending and shear strengths of fabricated spacers should be investigated for the case of spiral wound modules.

Other module studies

Differently from the spacer studies for flat or spiral wound membrane modules, Armbruster et al. focused on tubular modules, fabricating 3D printed static mixers with various geometries to promote turbulence for mitigating the fouling on ceramic membranes. A polyjet type 3D printer utilizing a photosensitive acrylate-based polymer as printing material and a second polymer as support material were employed to fabricate static mixers. Static mixers greatly enhanced the flux compared to membranes without static mixers, resulting in a wide range of transmembrane pressures that can greatly reduce membrane fouling. The best flux performance was observed for the Kenics static mixer which showed 140% improvement. However, pressure drops were also enhanced. The pressure losses by the “dots” mixer with a pitch length of 8.25 mm, the helix mixer with a pitch length of 8.25 mm, and Kenics mixer were 27%, 30% and 60% higher than the pressure loss of the pipe without static mixer, respectively; while static mixers with 13.75 mm pinch length had relatively less pressure drop [75]. This approach was further developed by the group with aerating static mixers which combines both air sparging and static mixing to mitigate fouling in tubular membrane filtration [76].

The accumulation of a retained component on the membrane’s surface is a critical problem that may significantly reduce mass transfer for hollow fiber membranes. Having a normal secondary flow on the surface is one solution for the concentration polarization and the fouling that cause the problem. In achieving this, it is important to have an optimum design for adsorbing momentum during the extrusion process. Therefore, the design and the bespoke fabrication of spinnerets is important. With regard to this point, Luelf et al. employed 3D printing to fabricate various spinnerets with different geometries [77].

In addition, 3D printing of microfluidic cross-flow filtration systems that Wardrip et al. implemented to provide feasibility for fouling studies is another novel approach to the application of membrane system technology. The microfluidic device operates with less test solution and can reduce the costs of foulants and compounds [78]. Another filtration system production was also introduced by 3D printing of a two-membrane single-pass module, which provides continuous, simultaneous concentration of retained (bio-)molecules and reduction or exchange of salt buffer [79].

Apart from spacer studies, there is not much research on other parts of membrane modules. Currently, most of the module studies are still based on computer modelling. 3D printing is a great opportunity for researchers to further validate their data for their previously completed research.

D printing applications for the fabrication of membranes

Fabrication of the membranes

Polymeric membranes. Although research into the fabrication of the whole membrane by 3D printing used to be rare, there have recently been various critical studies which began with an oil-water separation membrane as Lv et al. reported in their pioneering study [80]. They prepared superhydrophobic porous membranes for oil-water separation by 3D printing with nanosilica-filled polydimethylsiloxane (PDMS) ink. Prepared ink was printed through a homemade 3D printer having a computer-controlled 3-axis movement platform, a screw-driven fluid

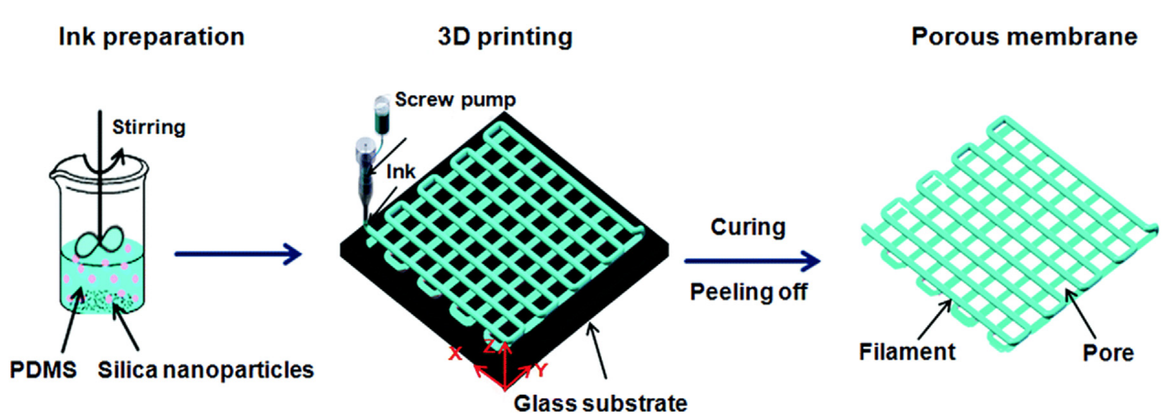

Fig. 4. 3D printing of a porous membrane with nanosilica-filled PDMS ink. The image is reproduced from a previous study [80] with the permission of Royal Society of Chemistry.

dispenser, and a micro-nozzle, typically with an inner diameter of 150 μm. Self-produced parallel PDMS filaments were uniformly printed on the PFTS-treated glass substrate to produce a consistent PDMS membrane that was heated at 120 °C for 1 h followed by peeling off of the substrate. As a result, a superhydrophobic surface on a porous framework was obtained by 3D printing, preventing weak interface adhesion, unlike the traditional methods (Fig. 4). Maximum oil-water separation efficiency (~99.6%) was obtained through pore sizes of 0.37 mm, which also exhibited approximately 23700 L $m^{-2} h^{-1}$ [80]. This study was followed by the study of Yuan et al. concerning oil-water separation [81]. Superhydrophobic polysulfone (PSU) membrane support was fabricated using a selective laser sintering type 3D printing technique. A single PSU powder layer was sintered to obtain the final 3D printed membrane. After coating the surface of the membrane with candle soat, performance tests were conducted. The membrane exhibited superhydrophobicity with a water contact angle of 161° and chemical stability when exposed to acidic, basic, and neutral solutions in addition to water. It also showed very high separation efficiency of over 99% for all of hexane/water separation even after 10 cycles [76]. Yuan et al. also synthesized 3D printed polyamide membrane with a superhydrophobic and underwater superoleophobic surface by modifying the surface with a rough, porous and micro/nano-structural Zeolitic imidazolate frameworks (ZIF-L). This approach provided a high oil rejection of over 99% with an oil flux of over 24000 LMH [82]. Through 3D printing, wavy supports for oil water separation membranes were also introduced to membrane literature [83,84]. A thin polyethersulfone (PES) layer was deposited on the 3D printed support, which was printed by a polyjet type 3D printer utilizing Visijet M3-X as printing material. This approach improved the

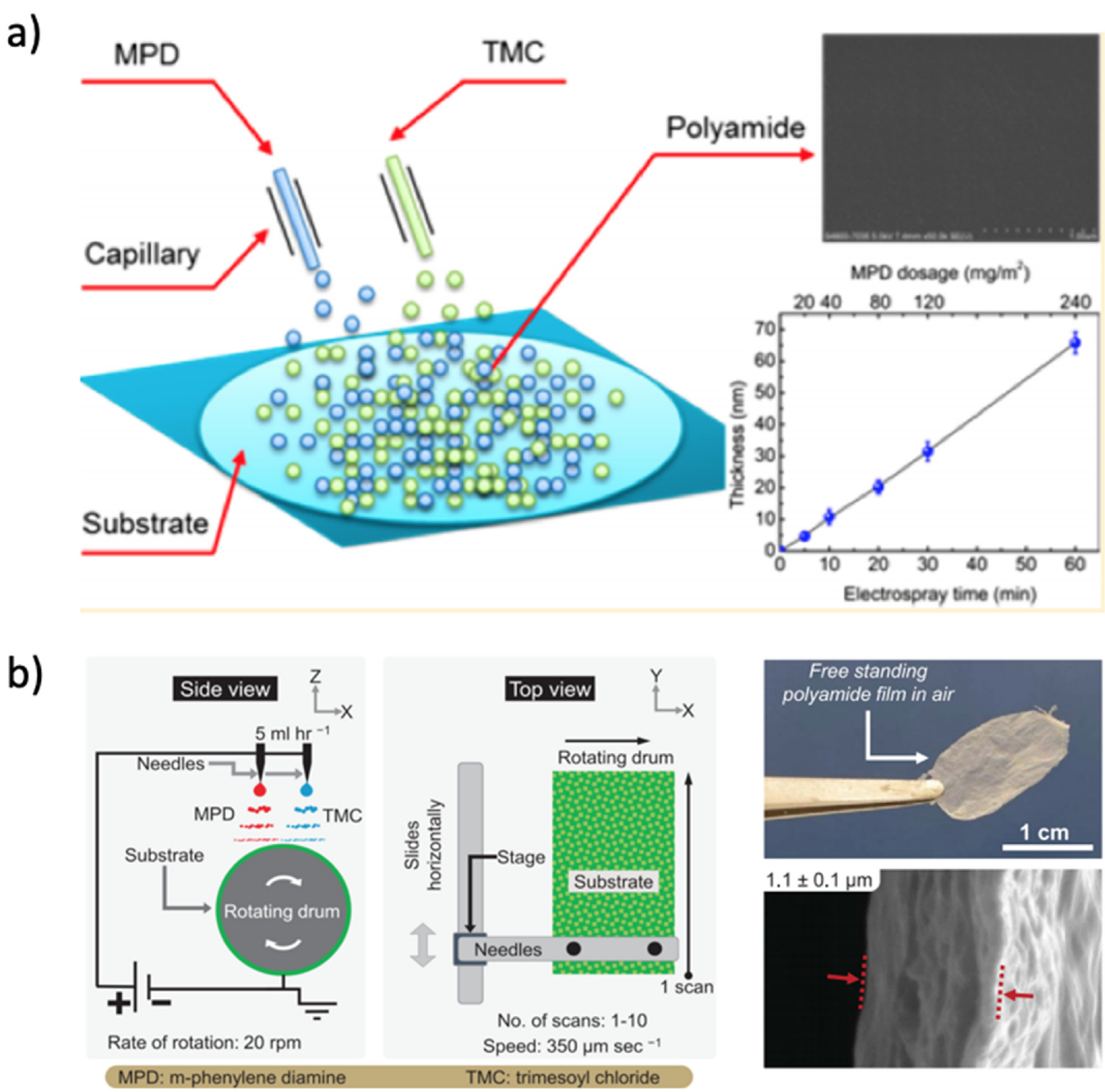

Fig. 5. **a)** Interfacial polymerization on the substrate through electrospraying (reproduced from a previous study [87] with the permission of the American Chemical Society)., **b)** Elecrospraying process for self-standing polyamide thin film (reproduced from a previous study [61] with the permission of the American Association for the Advancement of Science).

permeation, cleanability, and fouling build-up performances of the membranes. 52% higher permeance recovery, and 96% ± oil rejection ratios were observed. Same research group also applied the 3D printed wavy supports for cross flow ultrafiltration systems by using bovine serum albumin as feed solution. Pure water permeability and permeance recovery were enhanced by 87% and 53%, respectively [84]. Further approaches have been introduced by Li et al., with 3D-printed self-floating superhydrophobic and oleophilic membrane investigated by using robotic technology [85].

In addition to these studies on oil-water separation, there are some promising studies for other types of water treatment membranes. More recently, the use of 3D printed support for nanofiber membranes has also received a lot of attention. Koh et al. fabricated 3D printed polyethylene terephthalate (PET) supports for the fabrication of electrospun nanofiber membranes made of poly (methyl methacrylate)-graft-poly(dimethylsiloxane) (PMMA-g-PDMS) copolymer and polyamide 6 (PA6). The nanofiber diameter for the PMMA-g-PDMS copolymer was controlled under 0.437 μm with a surface layer thickness of 50 (±20) μm, while the diameter and pore size were 0.072 μm and 0.14 μm, respectively [86].

Thickness-adjusted layer by layer type electrospraying, which can be described as a simple version of 3D printing, was first applied by Tang's group [87] (Fig. 5a) and later improved by McCutcheon's group for 3D printing-assisted interfacial polymerization [61]. This research is important for the future of membrane science. In particular, Chowdhury et al.'s study not only creates a base research for the fabrication of self-standing 3D printed membranes but also the first application of 3D printing to the fabrication of reverse osmosis (RO) membranes. M-phenylene diamine (MPD) in water and trimesoyl chloride (TMC) in hexane were printed on the aluminum sacrificial surface by extrusions from separate needles (Fig. 5b). Depending on the scan number and the MPD-TMC ratio, the selectivity and the permeability were controlled successfully as a result of optimized thickness and pores. As a result of this procedure, polyamide (PA) films were fabricated with 20 nm thickness after five scans (average 4 nm per scan). The PA layer was applied on UF substrate for desalination purposes as well. The resulting thin-film composite (TFC) membranes showed 94% salt rejection and 14.7 LMH bar^{-1} permeance with a roughness of only 2.3 nm (five scans of MPD: TMC ratios of 0.083:0.05 on the PAN 450 UF membrane). This is less than one-sixth that of the SW30XLE membrane. Furthermore, higher rejection rates were achieved with different MPD:TMC ratios and scan numbers on the same UF substrate. However, this also resulted in the sacrifice of water permeability [61].

In addition to these studies, 3D printing technology is also useful in recreating structures that are inspired by nature, such as the eggbeater arm shapes that Yang et al. adopted as an energy-efficient oil/water separation solution [88]. This kind of biomimetic approach was also applied to membrane fabrication in the recent research of Xing et al. A lotus-leaf-inspired superhydrophobic porous PLA membrane was fabricated for oil-water separation using an FDM type 3D printer. The separation efficiency of 99.4% and 60 kLMH was obtained with a pore size of 250 μm [89].

Ceramic membranes. In contrast to the printing of polymeric membranes, Hwa et al. employed the technology to fabricate ceramic membranes for water purification (Fig. 6a). Particles sizes of 75, 150, and 250 μm of clay powders were used to fabricate 3D printed membranes. The clay membrane with 75 μm showed a 97.78% reduction in chemical oxygen demand (COD) and a 53.85% reduction in total suspended solids (TSS) because an interconnected structure created by small particles was effective in capturing the larger sized contaminants. Also, 3D printing provided high packing of the aggregation which enhanced the water quality in addition to the interconnected capillary network's capacity to attract water molecules [90]. Ray et al. brought another innovative approach to fabricating ceramic membranes by 3D printing. The research group employed the Solvent-based Slurry Stereolithography (3S) method. The 3S process differs from other 3D printing methods by its indirect fabrication approach, in which

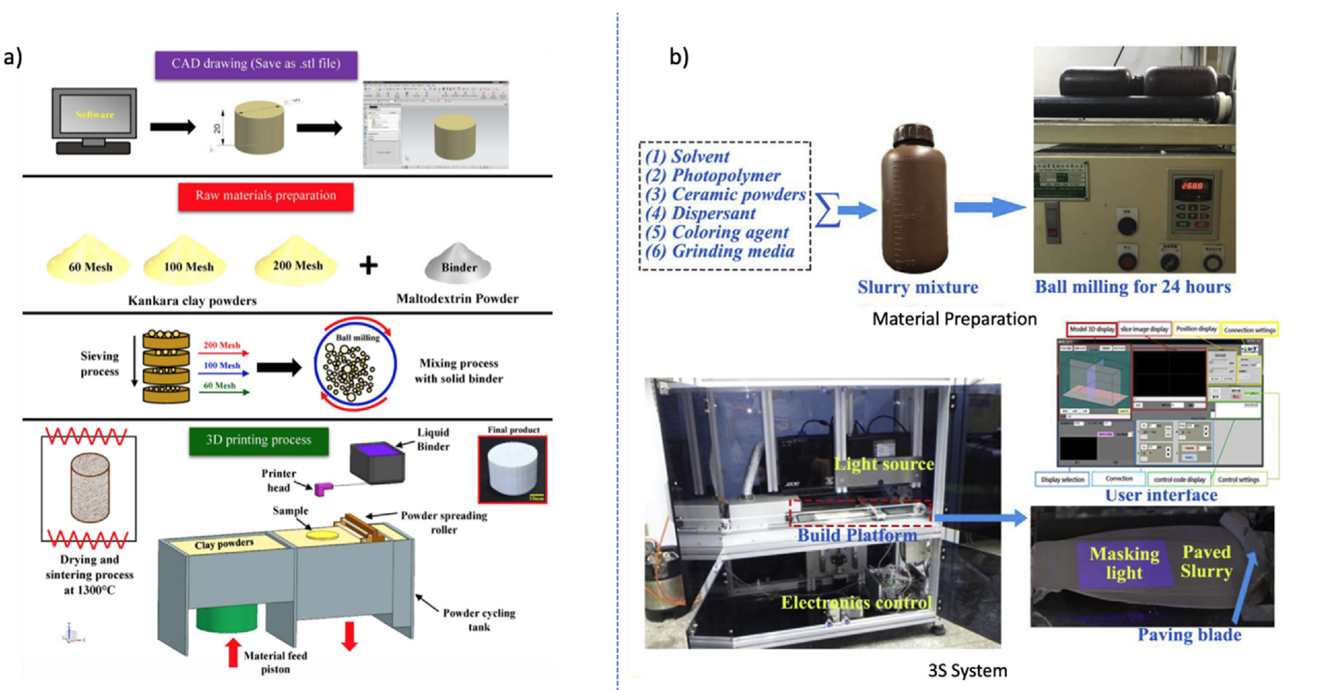

Fig. 6. Schematic diagram of the fabrication of ceramic membranes by 3D printing. a) Ceramic membranes made of clay powders and printed from a liquid blender (reproduced from a previous study [90] with the permission of Elsevier), b) Ceramic membranes made of alumina and printed by 3S process (reproduced from a previous study [91] with the permission of Elsevier).

densification by sintering process is done after 3D printing of the green parts. In the study, alumina material-based membranes were fabricated with a thickness and roughness range of 200−250 μm and 0.17−0.18 μm, respectively [91] (Fig. 6b). Even though membranes were fabricated successfully and proposed for ultrafiltration, filtration results should be further investigated to understand the convenience of the method.

Given the above studies on polymeric and ceramic membranes, the lack of technological integration between membrane science and 3D printing technology can be clearly seen. As 3D printing studies are not focused on the development of printers that can print polymeric or ceramic membrane materials. Most of membrane research is based on the utilization of currently available printing materials which are not highly efficient to use for filtration purposes. At this point, there is an urgent development requirement for 3D printers that can print membrane materials such as PAN, PES, PTFE, PVDF, Alumina, Titania, Zirconia etc. Furthermore, the development of printers that can adjust the amount of blending nanomaterial (CNT, Graphene etc.) is also another urgent requirement, especially for polymeric membranes.

Printing on membrane surfaces

The 3D printing technology to achieve a perfect fabrication of the whole membrane is still under development. However, more realistic studies based on current technology can be seen in the research regarding inkjet printing, or 3D printing of solvent or gel on the membrane's surface.

Inkjet printing. Inkjet printing is a type of printing onto paper or transparencies. Although it is widely used in industry, it was also adapted for scientific applications. As a result, research focusing on organic transistors, light-emitting diodes, ceramics, and biopolymer arrays has greatly increased [92]. There are two different types of inkjet printing: continuous inkjet (CIJ) and drop-on-demand (DOD) inkjet printing. CIJ printing works by producing a continuous stream of liquid drops and the unused ink is recycled by the deflection of an electric field. Although it is a sustainable process, the recycling stage carries the risk of contamination due to the exposure to the air. Unlike the CIJ type, the DOD type does not produce the droplets continuously. Therefore, it does not carry the risk of contamination by unused ink [93].

After inkjet printing technology began to be applied to the 3D printing of polymers and nanomaterials, it was adopted by membrane science and technology [94]. In particular, UF membranes have been the focus of research. Badalov et al. designed black and white checkerboard patterns by using Adobe Photoshop software and did an inkjet coating by printing a diamine monomer containing fluorine on a UF membrane pre-soaked in an aqueous solution of MPD, a commonly used membrane polyamide building block. As a result, enhanced performance for the membrane was obtained constituting the first effort to fabricate TFC membranes with patterned physical properties via printing assisted fabrication (PAF) methods. In the study, the incorporation of a patterned fluorinated diamine into an m-phenylenediamine-based polyamide yielded increased salt rejection in conjunction with selective layer hydrophobicity (Fig. 7) [95]. The study demonstrated the applicability of printing technology to interfacial polymerization. The same group of researchers applied this PAF method to the fabrication of polyamide film on a UF support without pattern creation [96].

The introduction of inkjet printing applications brought totally new approaches to the synthesis of a selective layer of water treatment membranes. Gao et al. developed the technology further using the synthesis of polymeric nanomaterials such as polymeric nanotubes, nanowires, and thin films [97]. For the synthesis of nanotubes and nanowires, a sacrificial template was prepared such as a polycarbonate track-etched (PCTE) membrane (Fig. 8). Deposition of material on the surface of the template was then carried out. In order to achieve the final form of the PCTE membranes, polymeric, carbon, metallic, and semiconducting materials were deposited inside the pores of the membrane to obtain nanotubes or nanowires. As a result, reasonable performance in terms of salt rejection and water flux was obtained for the inkjet-printed nanofiltration membranes [97].

Later, Gao et al. used the same approach, preparing poly (vinyl alcohol)-based composite inks containing poly (diallyldimethylammonium chloride) or poly (sodium 4-styrenesulfonate) to apply patterns with domains of ordered positive and negative charges to the surface of polycarbonate track-etched membranes. Having the same amount of positive and negative charge domains resulted in a neutral charge which increased the permeation of the mosaic membrane. Rejection rates of 17 ± 5% for the 1 mM feed solution and -2.0 ± 1.6% for the 10 mM feed solution were observed [98]. Differently from other researchers, Lee and Heo et al. utilized silver nanoparticles to print on electrospun polyurethane fibrous membranes using inkjet printing (Fig. 9). Silver nanoparticle printed membranes showed bacterial resistance during water purification [99].

Recently, Bernstein et al. utilized inkjet printing and graft polymerization surface modification of the polymeric membrane (Fig. 10a). In their research, polyethersulfone UF membrane surfaces were coated with [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide dissolved in base ink and then irradiated with UV light. The modified membranes resulted in low protein fouling properties and less biofilm growth (Fig. 10b) [100].

Since carbon-based materials, especially graphene-oxide (GO), were attracting a lot of attention on account of their highly

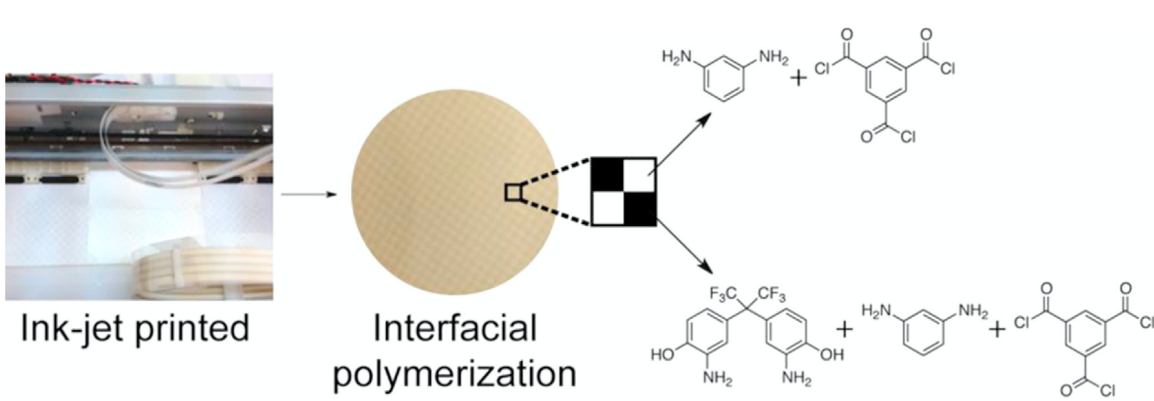

Fig. 7. Application of inkjet printing for interfacial polymerization. The image is reproduced from a previous study [95] with the permission of Elsevier.

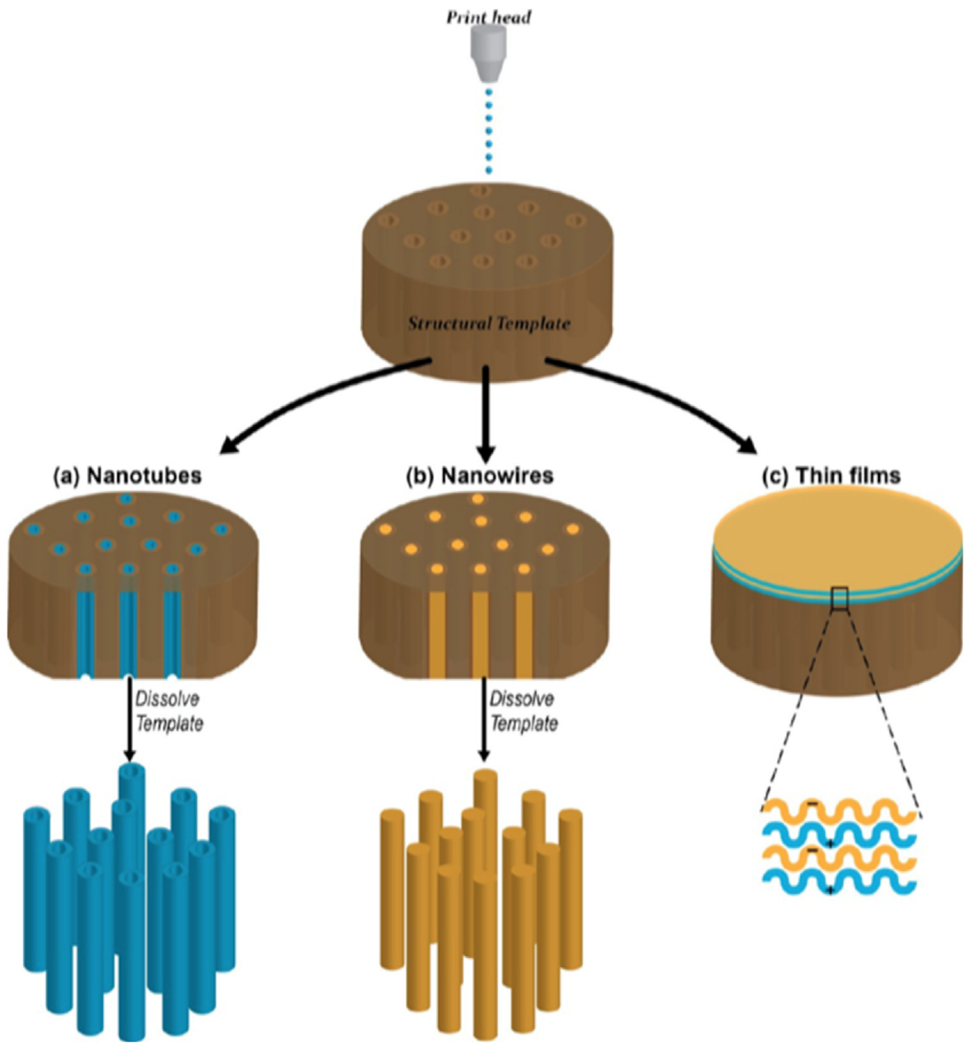

Fig. 8. Nanomaterials generated by inkjet printing and template synthesis. a) Polymeric nanotubes produced by printing PAH and PSS on a PCTE membrane template with vacuum b) Polymeric nanowires produced by simply printing PVA on a membrane template with a vacuum. c) LbL thin films on top of a PCTE membrane produced by printing layers of PAH and PSS without vacuum. The image is reproduced from a previous study [97] with the permission of American Chemical Society.

enhanced performance for water treatment membranes [101–109], Fathizadeh et al. used inkjet printing to obtain ultrathin GO membranes. GO "ink" was prepared by dispersing 400 mg of single-layer graphene-oxide (SLGO) in 100 mL DI water. After different concentrations of GO inks were prepared by dilution, a commercial printer was used to coat the M-PAN support with GO ink followed by drying procedures (Fig. 11). Through these simple procedures, ultrathin (7.5–60 nm) nanofiltration membranes were successfully fabricated. Although the 30 nm (two times printed) coating had the highest rejection rate for methyl orange (95.9%), the water permeance of the 15 nm (single printed) coating was double that of the 30 nm coating with a reasonable rejection rate of 83.9%. When the 30 nm coated (two times printed) sample with high rejection performance was tested for pharmaceutical rejection, it showed 76.4, 80.1, 83.0, and 95.2% rejection rates respectively for gemfibrozil, 17α-ethynylestradiol, diclofenac sodium salt, and iodixanol [110]. This research provides a sound basis for the future application of inkjet printing to other types of carbon materials such as carbon-nanotubes or graphenes to fabricate high-performance water treatment membranes. In particular, carbon-nanotubes are very well known for their high performance for water treatment membranes [111,112] and they have already been successfully applied to inkjet printing for CNT coating for various applications such as electronic applications [113–115].

Inkjet printing also has great importance for biomimetic applications. Surface modifications through inkjet printing can transform even superhydrophillic structures into superhydrophobic ones. Although it has not been applied to membrane fabrication, the study of Zhang et al. provides a suitable approach for surface modification. Zhang's group prepared a mussel-inspired ink consisting of an optimized solution of dopamine and applied inkjet printing to the production superhydrophobic surfaces inspired by the fog-collecting capabilities of Stenocara beetles in the Namib Desert. Superhydrophilic micropatterns were transformed into superhydrophobic surfaces by the formation of polydopamine via in situ polymerization. The micropatterned surface with a pattern size of about 500 mm and a separation distance of about 1000 mm showed 61.8 mg $cm^2 h^{-1}$ water collection performance from fog which is four times that of the unmodified one [116]. This approach to inkjet printing can be further applied to the creation of biomimetic superhydrophobic structures on the surfaces of water treatment membranes.

Solvent/Gel printing. Differently from inkjet printing, 3D printing with solvent or gel-based inks has also begun to be applied. These

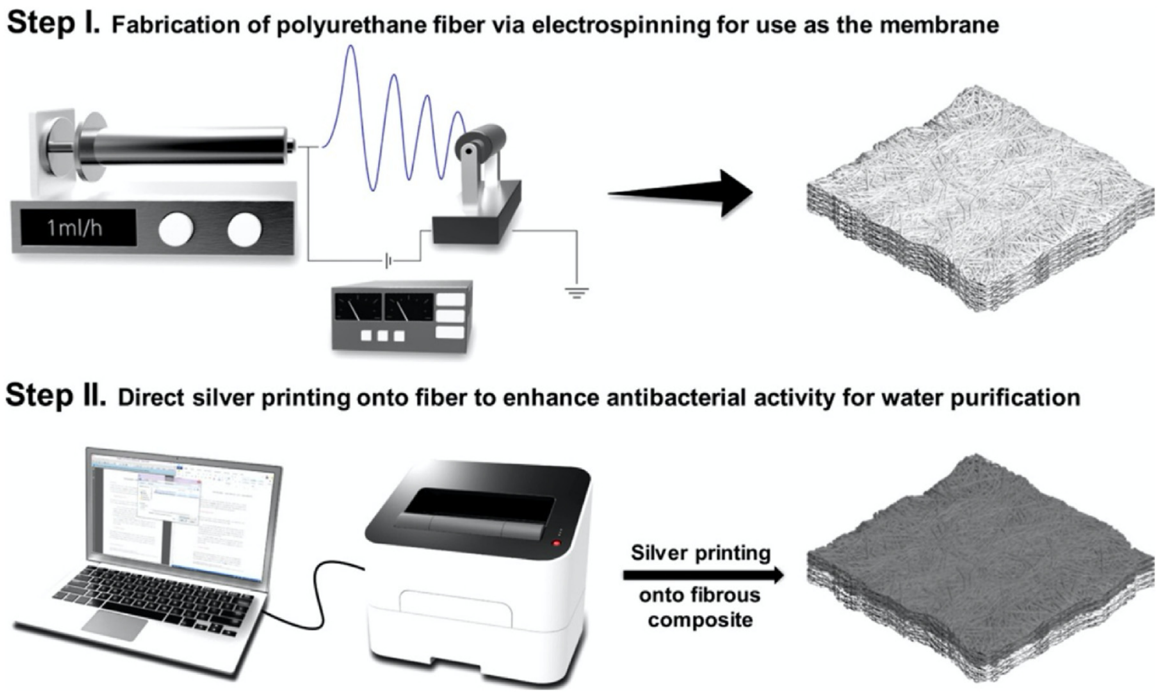

Fig. 9. The steps of the silver nanoparticle printing process on electrospun membrane. The image is reproduced from a previous study [99] with the permission of Elsevier.

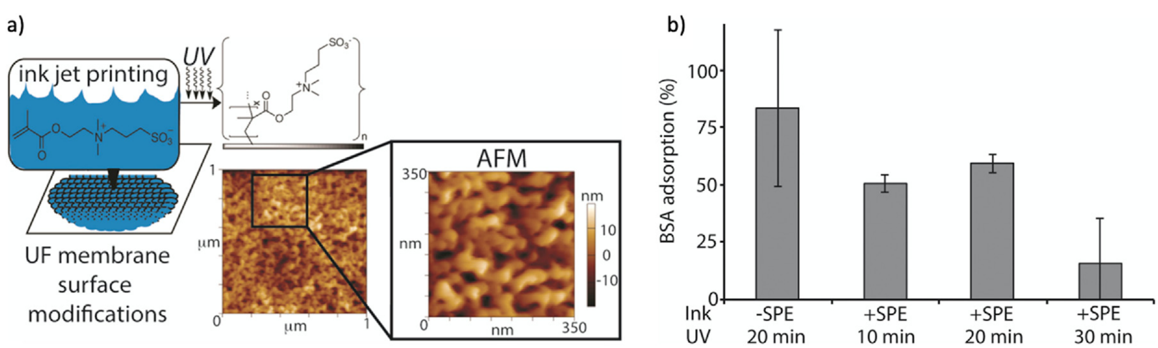

Fig. 10. a) Inkjet printing and graft polymerization surface modification of the polymeric membrane with an Atomic Force Microscopy (AFM) representation. b) Protein fouling (BSA) of UF membranes with 2 printed layers of 0.5 M SPE in base ink solution (UV-irradiated from 10 to 30 min). The image is reproduced from a previous study [100] with the permission of Elsevier.

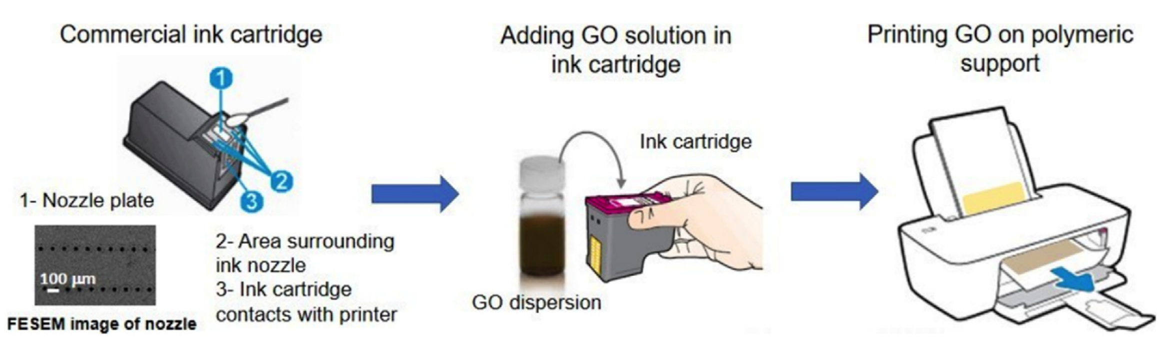

Fig. 11. Schematic diagram showing the procedure for printing ultrathin GO membranes. The image is reproduced from a previous study [110] with the permission of Royal Society of Chemistry.

types of printing provide a controllable pattern on the membrane's surface. He at al. applied this type of 3D printing to the fabrication of patterned carbon nitride–based hybrid aerogel membranes for solar wastewater remediation. g-C_3N_4 (CN) – sodium alginate (SA) inks were prepared by concentrating the mixture of CN nanosheets (CNNS) or CNNS/Au dispersion and an SA solution. After the aerogel had been prepared and the patterns programmed, 3D printing was carried out on a benchtop. Au/CN–SA aerogels with a ratio of CN:SA = 2:1 showed enhanced photodegradation with an efficiency of over 93%. It was also noticed that as CN:SA ratio increased, enhanced adsorption and photodegradation performance was observed [117]. Furthermore, electrospraying is a novel approach for printing nanomaterials on membrane surfaces as well. Chen et al. coated microfiltration membranes with GO to produce high selectivity nanofiltration membranes. In their research, as a result of GO coating, organic dye rejection rates of 98.88%, 98.97%, 100%, and 99.99% for basic fuchsin (BF), methylene blue (MB,), methyl orange (MO), and evans blue (EB) respectively and rejection rates of 63.13%, 27.86%, 41.82%, and 15.00% for Na_2SO_4, NaCl, $MgSO_4$, and $MgCl_2$ respectively were obtained with a high water flux of up to 20.23 LMH/bar [118].

As the anti-fouling or selectivity properties of membranes are mostly controlled by surfaces, surface printing technologies carry great importance to membrane science. Even though inkjet printing itself is not classified as a 3D printing technique, printing of 2D materials with designed patterns is the basis for all current 3D printed membrane research. When the above studies are seen, they all used commercial or conventionally fabricated supports. At this point, we can see clearly the need for research that combines both support and surface printing. In addition, advanced 3D printers that can do both surface and support printing without human interference should also be a considered technology to be worked on.

Perspectives and insights

Because 3D printing is still a developing technology, most of the research has been conducted at the micro or macro scale. However, the recent studies have shown that nanoscale research is also promising for the future of 3D printed water treatment membranes.

Because major studies have been carried out at the macro or micro scale, module design can be considered first. Most of the module studies have only focused on spacer fabrication. However, when we consider the whole module or a pressure vessel, a great deal can be done to enhance the performance of the filtration. The application of 3D printing would offer more realistic and versatile solutions than the research done by computer modelling. Moreover, it is important to fabricate the module parts and the pressure vessels with sustainable and non-toxic materials. Research concerning the 3D printing of cellulosic materials may open up new methods of fabricating membrane modules and pressure vessels from cheap and sustainable sources [119].

Regarding surface applications, various nanomaterials have been employed to coat membrane surfaces to create antifouling resistance or to enhance salt rejection properties, employing conventional wasteful methods. Therefore, technologies such as inkjet printing, electrospraying or solvent/gel printing on membranes' surfaces should replace these conventional wasteful methods. In addition, further surface applications such as melt electrospinning writing (MEW) should also be considered. MEW is a novel additive manufacturing technique that uses a computer-aided deposition process and allows the design and fabrication of micrometer-thin fibrous coatings [120].

When we consider the membranes themselves, major research has investigated oil-water separation or UF/NF membranes. As Chowdhury et al. fabricated first RO/UF membranes using 3D printing, his research approach into membrane distillation or forward osmosis/pressure retarded osmosis (FO/PRO) processes should also be considered. Fabrication of an active layer on the draw side of these osmotically driven membranes would highly enhance the fouling resistance. In particular, research related to PRO is important because this technology is only at the laboratory or pilot stage and needs to be accelerated to determine the applicable parameters before applying it to plant scale operations [121–125]. The application of 3D printing is vital for accelerating the research at this point in time. In addition, 3D printed hollow-fiber membranes should be considered as an alternative to current flat-type ones. This will also allow to control the inner surface parameters of hollow fibers, which is currently very difficult with conventional spinning methods.

When we consider them from a 3D printing perspective, new technologies are essential in achieving nanoscale fabrication for application to ion-selective water treatment membranes. Although 3D printing using 2 P P is capable of nanoscale printing, it cannot achieve less than 100−200 nm precision [24,126]. However, recent developments in 2 P P technology have potential for application to membrane science [127].

Another important focus of future research should be on biomimetic applications since 3D printing is a useful tool for imitating organic structures. Many fields of science have already benefited from this branch of research [128–130]. Although water harvesting research commonly uses 3D printing to create biomimetic structures [131], it is still not fully adapted to membrane-based water purification.

Furthermore, current studies do not have sufficient details about long-term performances. Therefore, it is as necessary to include long-term performances of 3D printed membranes. This would be better clarified through pilot scale studies.

Critiques and drawbacks

Although there are various advantages of 3D printing for the fabrication of water treatment membranes, there are still drawbacks mostly caused by the situation of the current technology.

Available 3D printers or 3D printing methods are capable to print with high resolution in z dimension. However, same precision cannot be obtained for x and y axis (Table 2). When we consider membrane structures, thickness and porosity carries great importance. Therefore, precisions in x, y and z axes should be very well controlled. Current precision in z scale is satisfying even for ultrathin membranes, porosity of membranes, which is dependent on x–y precision, is not easily controllable through 3D printing.

Another problem of current technology is the expensive 3D printer prices. Even though, the prices of FDM type printers are affordable, same thing cannot be said for other types of 3D printers. Especially, high resolution ones like polyjet or 2 P P type printers are very expensive even to afford their printing material

Long printing time is another drawback of the current technology. Even though 3D printing provides time efficiency through reducing failures and providing in-situ fabrication without having long transportation time, having a shorter printing would make 3D printing to be more convenient for the membranes for water treatment technologies.

Conclusions

3D printing has great significance for the future of membrane science with its sustainable, low-risk, precise, uniform, and relatively low-cost fabrication methods. However, although 3D printers were invented a long time ago and applied to other technologies, when we branch into the "nano" field, there is still some way to go. Therefore, achieving the fabrication of 3D printed water treatment membrane with nano-selectivity remains a critical goal.

However, as we have seen from the research, the fabrication of membrane module parts or modification of the membranes is an important step towards achieving the bespoke and precise production of future 3D printed membranes. Based on the current situation, we can comfortably say that, as commercial 3D printing technology reaches nanoscale precision, the rapid production of high ion-selective membranes will no longer be a dream.

Author declaration

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no unmentioned significant financial support for this work that could have influenced its outcome.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

Declaration of Competing Interest

The authors report no declarations of interest.

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