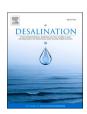
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3D printing for membrane desalination: Challenges and future prospects

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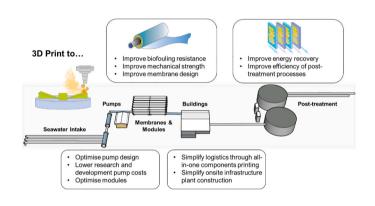
HIGHLIGHTS

- Applications for 3D printing across the entire desalination plant process was reviewed
- 3D printing costs are forecasted to decline by approximately 50-75% over the next decade.
- 3D printing will expand membrane, spacer, module, and plant designs and optimisations.
- 3D Printing will lead to lower operating, research, and engineering and procurement costs.
- Spacers lead commercialisation efforts for 3D printing in RO membrane desalination.
- 3D printing could potentially expedite the commercial viability of emerging desalination technologies.

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GRAPHICAL ABSTRACT



ABSTRACT

Recent years have shown a growing interest in the field of 3D printing for applications in the area of water treatment and desalination. The applications for 3D printing are applicable on numerous levels from membranes, spacers, modules, and entire plants; thanks to the high level of customisation, improving resolutions, low-cost to prototype and test designs, sustainability benefits, and reduced time and costs to fabricate new components for desalination. Previous review papers have discussed 3D printing for membrane desalination with a focus on membrane components and additive fabrication methods. This paper addresses the current limitations faced by 3D printing for water desalination and finally provides future perspectives that could address these barriers. The

Abbreviations: RO, Reverse Osmosis; FO, Forward Osmosis; MD, Membrane Distillation; CLIP, Continuous Liquid Interface Production; AM, Additive Manufacturing; SLA, Stereolithography; CAGR, Compound Annual Growth Rate; FDM, Fused Deposition Modelling; DLP, Digital Light Printing; UV-LCD, Ultraviolet Liquid Crystal Display; TFC, Thin-Film Composite; CTA, Cellulose Acetate; LMH, Litres per Meter Hour flux; PVDF, Poly(vinylidene difluoride); PDMS, Polydimethylsiloxane; PEI, Polyetherimide; VMD, Vacuum Membrane Distillation; GO, Graphene Oxide; PS, Polysulfone; PA, Polyamide; PES, Polyethersulfone; PPSU, Poly(phenyl sulfone); CN, Carbon Nitride; MPBF, Metal Powder Bed Fusion; SLS, Selective Laser Sintering; MJM, Multijet Modelling; MJP, Multijet Printing; DIW, Direct Inkjet Writing; 2PP, Two-Photon Polymerisation; 3DCP, 3D Construction Printing; UF, Ultrafiltration; NF, Nanofiltration; MF, Microfiltration; DCMD, Direct Contact Membrane Distillation; SGMD, Sweeping Gas Membrane Distillation; AGMD, Air Gap Sweeping Gas Membrane Distillation; BVUC, Build Volume Unit Cost; ABS, Acrylonitrile Butadiene Styrene; CFD, Computational Fluid Dynamics; TMC, trimesoyl chloride; MDP, m-phenylene diamine; 3S, Solvent based Slurry Stereolithography; CAD, Computer-Aided Design; CAM, Computer Aided Manufacturing; HM, Hybrid Manufacturing; LMD, Laser Metal Deposition; SLM, Selective Laser Melting; CNC, Computer-Numerically Controlled; PRO, Pressure Retarded Osmosis; G/CNT, Graphene Carbon Nanotubes; DPI, Dots-per-inch.

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primary goal for this work is to compare and review the current limitations faced by 3D printing technologies in membrane desalination and provide future perspectives in order to improve its adoptability in the industry. The identified barriers include: insufficient resolutions; build volume scale; production rates; appropriate materials; costs; mechanical strength; thermal, mechanical, and chemical stability, which are factors that impede the successful application of 3D printing in membrane water treatment and desalination. Meanwhile, future directions are proposed based on the current trends in membrane research and 3D printing technologies available.

1. Introduction

With a growing demand on the world's water resources and the potential economic impacts on the failure to tackle this problem, governments around the world are finding solutions to safeguard this precious resource. According to the World Bank, climate change has induced water shortages that could cost a country up to 6% of their Gross Domestic Product, heighten the risk for conflicts, force human migration between different regions, increase risks for droughts, and raise food prices [1]. Desalination is one solution to this issue which capitalises on the vast water reserves of the ocean that covers 70% of the world's surface - however, less than 3% of this is drinkable and 2% of it is actually frozen [2]. Cumulative freshwater consumption rose from 46.6 million m³ per day to 67.3 million m³ per day between 2005 and 2009 [3], proportionally with the growth in population, infrastructure, and industrialisation. By 2017, the daily water consumption rose to 99.8 million m³ per day [4]. This strain on water supply has prompted a need to develop innovative technologies that will improve global water supply, affordability, and accessibility.

Research into 3D printing for membrane desalination has garnered growing interest over the past years. Conducting a bibliometric analysis using SCOPUS to identify the trends and with the key search terms TITLE-ABS-KEY ("Water" AND "Membrane" OR "3D Printed" AND "3D Printing"), the number of articles published has grown (Fig. 1). The topic of 3D printing for membrane desalination has grown interest particularly in the area of membrane feed spacer design. Although this area of research is still in its infancy stages, the application of 3D printing technologies in improving water treatment and desalination technologies remains highly promising due to the limitless applications in the design and optimisation of membrane modules and spacers.

Since its inception in the mid-1980s, 3D printing has had a beneficial impact on a wide range of industries. Stereolithography (SLA), fused deposition modelling (FDM), and digital light processing (DLP) are the three major 3D printing technologies which are forecasted to dominate the defence, healthcare, pharmaceutical, automotive, and aerospace industries [5]. These industries will seek to use 3D printing for a wide range of benefits. The technology - when applied to the membrane desalination industry - could reduce energy demands for desalination processes by between 15 and 20% due to more efficient membrane designs [6], lower manufacturing energy demands by 50% [7], lead to more environmentally friendly and easier to maintain equipment [8].

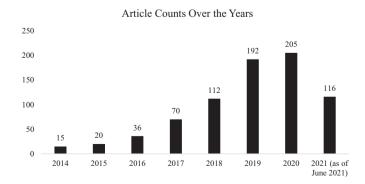


Fig. 1. Quantity of articles by year published relating 3D printing technologies to water desalination.

The use of ash and slag [9], biodegradable materials [10–12], recycled 3D printing material [13], and wood fillings [14] are other environmental advantages from using 3D printed materials. 3D printing for manufacturing has the potential to reduce costs of between US\$ 170–595 billion, energy consumption by 2.54–9.30 EJ, and $\rm CO_2$ emissions by 130.5–525.5 MT by 2025 [15]. The adoption of 3D printing technologies for membrane desalination is still in its early research stages, while the industry still grapples with its widespread adoption.

From 2010, the market for 3D printing grew at an average rate of 27.4% to \$12.8 billion in 2020 [16]. In 2021, it is expected that the 3D printing market will grow by 23.2% [17] and forecasted at a compound annual growth rate (CAGR) of 14–23.5% until 2027 [5,18]. Nanosun, one of the earliest pioneers to use 3D printing electrospinning techniques to commercialise its membranes, have so far serviced 15 plants [19]. Unlike conventional 3D printing, electrospinning does not produce finely controlled features and its concept has been around since the late 1800s, with publications only beginning to exponentially grow commencing 1995 onwards [20]. Nevertheless, 3D printing is expected to become an essential technology for organisations looking to gain economic and environmental benefits for the foreseeable future.

Currently, 3D printing applications towards membrane desalination is a new area of study that is gaining traction, with the majority of studies done towards spacers [21-27]. 3D printed spacers have been found to reduce fouling and scaling, promote flux by creating higher fluid flow unsteadiness and shear stress. Feed spacers with complex geometries were designed to optimise the membrane channel hydrodynamic that would otherwise have been impossible to fabricate using conventional means. The combined use of fluid dynamic models to determine the design features and geometries [28,29] provides a topological blueprint for further fabrication and enhanced crosscompatibility with other membrane components down the supply chain. To date, there are no studies conducted solely on 3D printed membrane modules across all types of desalination technologies despite the potential with current AM; and no successfully and commercially made 3D printed membrane which utilises conventional 3D printing technologies has ever been achieved. Meanwhile, 3D printing for spacers and infrastructure [9,30,31] do exist, although very few literature sources exist for modules and 3D printing desalination membranes due to its technically limitations.

Many technologies have been proposed in the fabrication of membranes, however, currently the production of membranes remains out of reach due to the small pore sizes required on the order of less than 1 µm. Tumbleston et al. [32] proposed the use of Continuous Liquid Interface Production (CLIP) for much larger production of parts. This eliminates any potential defects resulting from the presence of air bubbles compared with DLP technologies where the platform is lifted out of the vat resin bath and then resubmerged into the resin solution for another layer to be cured. This production technique was also proposed for the fabrication of membranes by Mecham et al. [33]. CLIP allows for the potential to fabricate membranes to infinite lengths and unlike DLP, does not require any stoppages to separate repeating parts from the base platform. Unlike DLP where entire flat sheets can be cured using a UV-LCD screen, a major limitation with using CLIP is the Z-axis vertical layer build time as opposed to the layer curing times inherent within DLP systems which is still low. For modules, where resolution requirements for current 3D printing technologies are not a barrier to its fabrication [34], the technologies exist for a wide range of applications but are not

Substrates	3D printing technology	Additive description	Print resolution	Advantages	Disadvantages	Desalination	applications	:		
through movable nozale. Consulvarials are printed stacked to create final model.			XY/Z			Membranes	Spacers	Modules	assets (i.e., pipes and	Major infrastructural assets (i.e., buildings and water tanks)
Digital Light Processing (DLP) Vis Green pixels cure 15-100/5-25 High micrometre Low build volumes and	3D Construction Printing (3DCP)	through movable nozzle. • Contours/trails are printed stacked to create	>1000 μm	Readily use cement	High cost. Inconsistent structural integrity. Requires correct viscosity	×	×	×	×	/
material onto surface substrates or polymers sective droplets. Fused Deposition Modelling (FDM)	Digital Light Processing (DLP)	photopolymer resin. • Cured every layer along			scalability. Limited to materials curable by UV light.	/	×	×	×	×
Fused Deposition Modelling (FDM)	Direct Inkjet Writing (DIW)	material onto surface. • Substrates or polymers		e., office printer). High scalability.	Bonding strength dependent on surface	✓	×	×	×	×
Selective Laser Sintering (SLS) are sintered together. • High-powered lasers used to sinter. • Roller replenishes process. High require further • Roller replenishes process. High gover and be reused. • Roller replenishes process. High gover and be reused. • Roller replenishes process. High gover and be reused. • Roller replenishes process. High gover and be reused. • Roller replenishes process. High gover and be reused. • Roller replenishes process. High gover and be reused. • Roller replenishes process. High gover and be reused. • Roller replenishes process. High gover and be reused. • Roller replenishes process. High gover and be reused. • Roller replenishes process. High gover and be reused. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited and cured with UV light every layer. • Wax droplets deposited ever	Fused Deposition Modelling (FDM)	 Thermoplastic extruded through heated nozzle. Nozzle lays polymer trails for every Z-axis. Layers of stacked trails/contours create final 		Low-cost and scalable. Printer simple by construction. Wide range of	Low resolution. Porosity affects mechanical strength and swelling.	/	/	1	/	×
Multijet Modelling (MJM)/Multijet Printing (MJP)/Polyjet And cured with UV light every layer. Hardness adjusted Support material can ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓ ✓	, ,	are sintered together. • High-powered lasers used to sinter. • Roller replenishes	300/100 μm	geometries. Use of metallic alloys with corrosion resistance. Little to no support required.	May require surface treatment for corrosion resistance. May require further surface finishing. Lower mechanical strength than subtractive processes. Energy intensive.	•	/	/	/	×
consistency across model.		and cured with UV light		through feed mixture ratios. Suitable for creating composite models. Good surface finish. Wide range of colours. Good chemical resistance. High mechanical consistency across	Support material can cause undesirable properties. Cannot produce sharp corners. Strength dependent on additive polymeric binder.	,	•	✓	×	×

3D printing technology	Additive description	Print resolution	Advantages	Disadvantages	Desalination applications	pplications			
		Z/XX			Membranes	Spacers	Modules	Membranes Spacers Modules Minor infrastructural assets (i.e., pipes and turbines)	Major infrastructural assets (i.e., buildings and water tanks)
Stereolithography (SIA)/vat- photopolymerisation/micro- stereolithography (MSLA)	Laser spot cures resin for 25–50/25–300 each layer Platform moves down Z-axis after each curing.	25-50/25-300 μm	High micrometre resolution. Good surface finish.	Toxic resins. Low mechanical strength. Low thermal resistance. High capital cost for	`	`	`	×	×
Two-Photon Polymerisation (2PP)	 Resin is cured at the electron-scale. Sum of two-photons being absorbed within lead to curing. 	$<1/<1 \mu m$ $\sim 0.2-0.3/$ $\sim 0.2-0.3$ (specified)	High nanometre resolution.	targer printers. Cannot produce large models. High capital cost.	`	×	×	×	×

studied due to the established existence of RO modules and the temperature sensitivity of 3D printing polymers for membrane distillation (MD).

Previous review articles have examined the applications of 3D printing at a component level, with focuses being on membranes, spacers, and modules. These review papers [34-40] discuss the applications of 3D printing for membrane desalination from a manufacturing perspective and how these could be applied to the fabrication of membranes, modules, and spacers. Where prototyping and advanced additive manufacturing techniques could expand the prototyping and design capabilities of 3D printed components for membrane desalination plants, no such review paper has yet to discuss the implications of 3D printing on entire desalination plants across pre-treatment, membrane reverse osmosis, and post-treatment stages. Currently, 3D printing research interest is more focused on the development and design of improved desalination performances at the lab-scale by changing spacer and membrane characteristics, with no study to date solely focusing on 3D printed modules and its impacts on desalination for other membrane desalination technologies apart from RO. This review paper examines and discusses the key barriers 3D printing faces during its applications towards membrane desalination, while providing future directions on what current research activities in this space can deliver to an entire membrane desalination plant. This review paper is unique in that 3D printing technologies have rarely been discussed with its wider applications towards desalination plants throughout its system, despite the rapid growth and importance being put on 3D printing by companies to reach environmental and economic objectives. Another unique dimension to this review paper is that it identifies barriers across membrane, component, and plant assets encountered when adopting 3D printing technologies. This paper also provides future directions to current research with 3D printing applications on overcoming these barriers, leading to benefits for operators of the desalination plant that is realisable from construction to its operation.

2. Overview of current 3D printing technologies used for membrane desalination

Over the years there has been a shift towards the use of lasers to cure resins at high precisions and resolutions and resolutions. Although, FDM continues to remain the cheapest form of 3D printing technology for the fabrication of larger components requiring less stringency on resolution, while laser-based 3D printers are used for the design and fabrication of intricate models. 3D printing technologies can be categorised, and have been applied in the following [41–48] seen in Tables 1, 2, Figs. 2 and 3.

2.1. Barriers and benefits towards additive manufacturing for membrane desalination

There are of course, several challenges facing the use of 3D printing for direct membrane fabrication. Although, electrospinning could be considered a form of 3D printing technology, the lack of direct controllability for the membrane's morphological features is a primary limitation where generally, only the thickness up to a certain point can be controlled. It is the poor resolution, limited selection of materials, slow printing, high costs both recurring and upfront, safety and environmental concerns, and industrial scalability barriers: that all pose challenges to its wider adoption in the membrane fabrication industry [35]. 3D printing using ceramics have several limitations including direct printing control of the membrane morphological and topographical features compared with thermoplastic- and photopolymerbased printers. Like polymer-based 3D printers, the high costs, low resolutions, and the infancy stages for this technology are what prevent it from advancing to a more mature technology status. For all 3D printers, the advantages allow for the fabrication of membranes outside the traditional designs of flat sheet, tubular, and hollow fiber configurations, and the possibilities to design, optimise, redesign, retest, and

 Table 2

 Recent membrane desalination research papers dealing with 3D printing technologies and the challenges, advantages, and disadvantages encountered.

Application (part)	Manufacturing method	Solutions to overcome membrane challenges	Advantages	Disadvantages	Source
AGMD (spacers)	SLS	Complex spacers and features printed.	Reduced cost of spacer fabrication.	Lower membrane costs insensitive to water production cost.	[49]
DCMD (spacers)	SLS	Complex spacers and features printed.	Improved turbulence. Sustained flux across high salinity ranges.	Wetting detected across membrane.	[29]
DCMD (spacers)	SLS	Complex spacers and features printed.	Reduced scaling. Improved monitoring for scaling. Improved flux.	Lower pressure drop penalty.	[28]
DCMD (spacers)	Selective Laser Sintering (SLS)	Complex gyroid features printed into spacers.	Reduced fouling deposition on membrane. Reduced fouling deposition on spacer.	Only delays inevitable scaling.	[27]
Filtration (spacers)	DLP	Complex spacers and features printed.	Improved flux. Lower energy consumption/ reduced fouling.	Potential localised fouling.	[50]
Filtration (spacers)	MJM	Microfabrication of spacers.	Improved flux. Micro-features produced.	Increased pressure drop.	[51]
FO (spacers)	MJM	Complex, biodegradable spacers fabricated.	Reduced fouling (PLA). Improved flux (ABS).	Polymer swelling (ABS). Lower resolution (PP).	[52]
FO (spacers)	MJM	Complex spacers and features printed.	Reduced reverse salt flux. Reduced fouling. Simple cleaning.	Residual foulants remain after cleaning.	[53]
Membrane manufacturing components (bore)	SLA	Complex membrane manufacturing components printed.	Improved packing density.	Complex mixing procedures for correct extrusion.	[54]
Microfiltration (spacers)	FDM	Computer optimised, complexly printed spacers.	Improved flux. Reduced fouling. Reduced caking/scaling. Dead zone elimination.	Can also lead to high cake formation (circular spacers).	[55]
Nanofiltration (spacers)	SLS	Complex spacers and features printed.	Reduced fouling. Improved flux. Improved turbulence.	Gradual flux decline.	[26]
RO + ultrafiltration (spacers)	SLS	Complex spacers and features printed.	Lower pressure drop. Improved flux.	Localised fouling.	[24]
Ultrafiltration (spacers)	Digital Light Processing (DLP)	Design with computational optimisations.	Improved turbulence. Improved flux. Reduced fouling deposition on spacer.	Only delays inevitable scaling.	[56]
Ultrafiltration (support layer)	MultiJet Printing (MJM)	Complex spacers and features printed.	Improved turbulence. Improved flux. Improved flux recovery after cleaning.	Extensive cleaning.	[57]
Ultrafiltration (membrane)	SLA 3D printing with ceramic using alumina bonders.	3D printer controlled ceramic thickness.	Environmentally friendly. Control membrane thickness.	Pore closures. Trade-off between mechanical strength and pore closures.	[58]
VMD (baffles)	Stereolithography (SLA) 3D printing using Formlabs.	Design with computational optimisations. Experimental simplification.	Reduced temperature polarisation. Reduced thermal energy loss. Improved flux. Critical flow identification.	Crystallisation	[59]

deploy at much cheaper costs compared to subtractive or chemical reactions. 3D printing with embedded ceramic materials have been done in the past using alumina and silica nanoparticles in membranes [60–63], although the use of ceramic as a general material in all aspects of desalination is costly compared to its polymeric counterparts.

The barriers to 3D printing vary depending on the type of application. For thermal-based desalination, temperature resistance will be a highly desired property for the printed component. Meanwhile, in pressure-driven desalination, mechanically strong and stable components will take high priority. For membranes, superhydrophobicity will find better applications for MD compared to RO, where hydrophilic materials are needed. However, throughout all membrane desalination applications, the universal barriers to the application of 3D printing are resolution, cost, industrial scalability, and chemical stability. Much larger components will find less importance in resolution such as modules and water tanks, while resolutions in fabricating membrane pores

and microfeatures that produce reliable sources of safe, drinkable water will be extremely important.

2.1.1. Cost

The design and production of complex 3D printed membrane desalination components paves way for economically beneficial opportunities for the desalination industry's plant operators and membrane manufacturers. A recent study cites that the cost of SLS and FDM 3D printed parts can be reduced by 10% and 70–80% respectively when polymeric feed materials are reused in the circular economy [64]. Taking advantage of the increasingly sustainable reuse of 3D printer polymeric materials, membranes can then be reformed into complex shapes that prolong the operating life of membranes and minimise cleaning frequencies and costs. However, the use of virgin plastics for 3D printing is still some of the most expensive, costing around \$US250/kg for FDM printers [38], while the printers can cost a lot more on the order

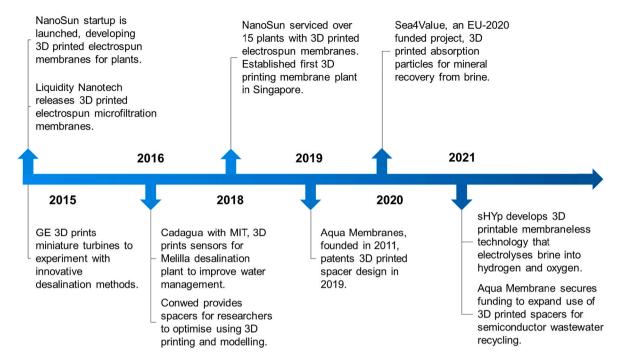


Fig. 2. Timeline of 3D printing applications within desalination and other related applications.

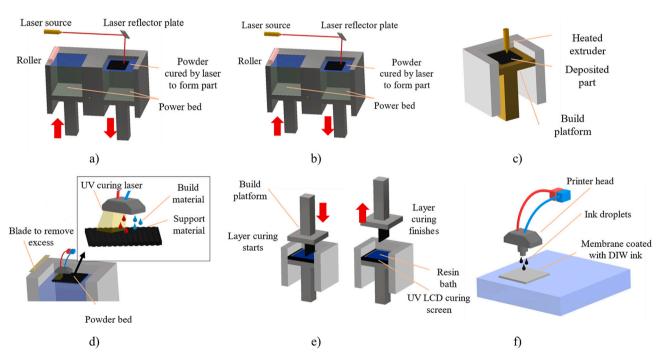
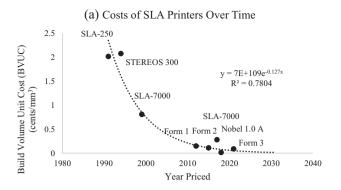


Fig. 3. a) Selective Laser Sintering (SLS); b) Stereolithography (SLA); c) Fused Deposition Modelling (FDM); d) Multijet Modelling/Multijet Printing (MJM/MJP); e) Digital Light Processing (DLP); f) Direct Inkjet Writing (DIW).

of several thousand dollars. Meanwhile, productivity improvements through the use of 3D printed spacers can be as high as 93% [51], indicating that the main benefits will arise from the long-term savings that 3D printed spacers can have on desalination systems such as the specific energy consumption, flux, and minimal cleaning maintenance.

The direct fabrication of membranes using 3D printing is still a farfetched reality. When compared with phase inversion and electrospinning, 3D printing loses out in terms of material consumption costs, build time, and resolution. Depending on the type of desalination, flawless nanometre resolutions are required with the general trend that the higher the resolution for a 3D printer, the more expensive it becomes. Presently, the Photonic Professional GT2 can cost half a million euros to procure with very little productivity gains, with the suppliers citing that to fabricate a membrane it will take 24 days per mm³ volume of printing as quoted by Nanoscribe. This is given that the resolution of the printer is rated at 400 nm and costs around \$500,000 [65]. This becomes an uneconomically feasible feat for membrane fabrication, and there is a long way ahead towards 3D printers capable of printing repeatable parts at nanometre resolutions that are necessary for RO applications. While DLP printing is a more promising alternative, which



(b) Costs of DLP Printers Over Time Build Volume Unit Cost (BVUC) 4.5 4 3.5 = 6E+241e^{-0.277x} 3 Perfactory = 0.56492.5 2 Max 1.5 Sonic Mini 4K Titan 2 HR Photon Zero 0.5 0 2005 2010 2015 2020 2025 2030 2035

Year Priced

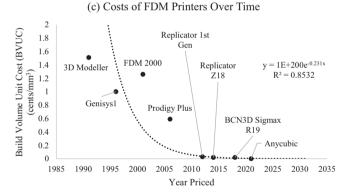


Fig. 4. Prices for 3D printers have dropped exponentially over the past \sim 35 years, with this trend expecting to continue leading to a reduction in printing costs by 50–75% by 2035 ((a) Costs of SLA Printers Over Time, (b) Costs of DLP Printers Over Time, (c) Costs of FDM Printers Over Time).

cures photopolymeric resin on a layer-by-layer basis. However, the smallest resolutions on the order of 15–25 μm are presently available on the market for such printers (Kudo3D Micro SLA and MakeX PRO25 DLP printers), currently cost between \$8700–\$US10,000 [66,67], and have maximum build volumes of around 48 mm \times 27 mm for both – too small for any commercial application. Presently on the market, FDM printers are some of the cheapest 3D printing technologies that can be purchased and experimented with previous studies [68–70], allowing more macroscaled experiments towards membrane desalination to be done. FDM parts were found to contain the lowest resolution, however, FDM is regarded as the most affordable form of 3D printing technology on the market with prices falling from \$US50,000 from nearly 30 years ago to around \$US300 today [70].

It is forecasted that the cost of 3D printers will decline in the coming years just as it has been for the past three decades. The reduced costs in 3D printing make it an economically attractive technology for the production of high-resolution membranes requiring complexity at the

micro-scale. During the emerging period for 3D printing, the cost of printers can cost from \$10,000 all the way up to \$500,000 [71]. Over the next decade, it is estimated that the cost of 3D printing will be reduced by between 50 and 75% from the current costs (Fig. 4). In these cases, the costs should not increase while increasing the build volume of the printers and its resolutions. The decline in build volume unit costs (BVUC) was more pronounced in DLP printers falling from 3.25 cents/ mm³ with the EnvisionTEC Perfactory to 0.03 cents/mm³ between 2007 and 2021 – a factor of $\sim \! 110$ reduction. Compared to SLA with the technology being present for longer than FDM, the BVUC has fallen from around ~2 cents/mm³ to 0.002 cents/mm³ in the space from 1991 to 2018 - a reduction of 1000 in magnitude. FDM started off with lower BVUC and gradually declined to half the costs compared to that of SLA, from 1.51 to 0.001 cents/mm³ – declining by a factor of \sim 1500 in the period. It is expected that these exponential trends will continue into the future with the affordability of 3D printers becoming a reality for manufacturers, however, scalability in terms of size and production quantities becomes a real limitation facing 3D printing applications towards membrane fabrication.

2.1.2. Thermal stability

Polymers offer the most affordable option compared with ceramic materials due to the lack of a need for post-processing (such as sintering). However, there are disadvantages to its use at the microfabrication scale in thermally driven desalination environments. Fig. 5 shows the before and aftereffects of rapidly exposing a DLP 3D printed membrane to a hot feed solution at 50 °C. On the contrary when the feed solution was slowly heated such micro fractures were averted. This presents a limitation for the application of 3D printing membranes in thermally driven membrane desalination systems, where for every operation, the feed solution must be slowly heated to prevent the thermal stressed induced within the micro-structures of the 3D printing membrane. The use of thermoplastics in 3D printing membrane fabrication makes it vulnerable to thermally driven processes, leading to significant membrane warpage and catastrophic failure over longer periods of operation.

2.1.3. Mechanical strength

Mechanical strengths among polymeric printers are substantially weaker compared with SLS using metallic powder as the membrane material. The material's bulk modulus for expansivity, the durability of the material when submerged in water for long periods of time, and whether hydrolysis can occur are key considerations in the use of membranes for desalination. Due to the sintering behaviour of powders the resolutions of 3D printers would be lower compared with thermoplastic- and photopolymer-based 3D printing technologies. This is because the SLS principle depends on the size of the power particles and the laser spot size, with typical SLS resolutions being around 70–100 μm and powder particle sizes of 5–20 μm [72–74]. This makes it highly compatible with the design and fabrication of spacers and modules that are mechanically sturdy but do not require extremely detailed features.

Wittbrodt and Pearce [74] studied the effects of colour and strength of the 3D printed part. The variations in crystallinity within the part were a cause for concern where non-uniform 3D printed structures were more susceptible to mechanical failures. The orientation of internal structures for a printed part were evaluated by Letcher and Waytashek [75], the printed tensile strength for a 45° raster component was 64 MPa, compared to 0° and 90° raster orientation and a tensile strength of 58 and 54 MPa respectively. Mechanical strengths were also determined by the thickness of the printed layers [76,77], where smaller thicknesses led to higher mechanical strengths. Wittbrodt and Pearce [74] study highlights the importance that the addition of chemicals plays in altering the internal crystalline structure for a 3D printed part. In membrane desalination, it is highly unlikely that colour will be important, however, chemicals that improve the hydrophobicity or hydrophilicity of a component must not be used to the detriment of

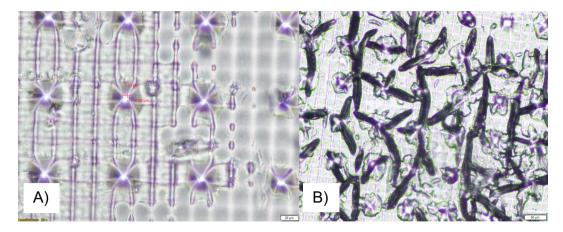


Fig. 5. (a) Intact membrane before the MD operation. (b) 3D printed membrane after being subjected to thermal stresses from the MD operation. 3D printed MD membrane was fabricated in our lab.

mechanical strength. These include the formation of voids which can lead to long-term degradation in mechanical integrity [13,78]. Designers of membrane components can experiment with the different layering and structural designs using their printers and smaller layer thicknesses may help alleviate some of the weaknesses arising from the development of resins that print mechanically weak, amorphous structures. Consequently, smaller layer thicknesses and higher fill volumes lead to longer print times, leading to lower productivity and commercial viability. Mechanical sturdiness is determined by layer thicknesses, print times, chemical additives used, and the design of internal structures for the printed part. Mechanical strength will strongly influence the selection process for viable resins and printing technologies.

Post-processing steps can be taken to improve the mechanical strength of a 3D printed part. In DLP and SLA printing, parts can be cured under UV light for a period of time. Longer curing times improve the mechanical strength for the part and was demonstrated in Kim et al. [79] when curing times were raised from 60 to 90 min, leading to an improved flexural strength from 120.93 MPa to 131.94 MPa. Raising the curing time will lead to greater brittleness of the printed model, which is undesirable for fabricating modules which require high flexural strength [80]. Changing the printing conditions such as raising the resin bath temperature and reducing its viscosity can lead to stronger prints [81]. The disadvantage to using this approach is reduced resolution due to the resin's lack of affinity for separation from the printed part after each curing stage, leading to unwanted cured features. Resolutions for membrane modules need only to be sufficient enough to prevent the leakage of water during pressurisation. While smaller detailed features such as membranes will face significant challenges in producing highly detailed nanoscale features combined with high mechanical strength comparable to composite, asymmetric, and symmetric RO membranes. Another barrier is the rigidity of the models that can be fabricated. In some cases, flexibly rolled membranes for example, are desired in RO when fitted to standard cylindrical modules, while plate-and-frame designs are more feasible for flat membranes. Given that the RO industry has followed the same module design conventions, the fabrication of membranes with consistently high flexural strength for example, poses another barrier. Table 3 shows the range of printing materials available, including the metallic alloy Inconel and 2PP materials exhibiting the greatest thermal resistance properties in the table. A combination of uniquely developed 3D printing materials that is crystalline combined with strong cross-sectional design for printed components are some solutions to overcoming barriers relating to low mechanical strength. The pressures required to be withstood for RO membranes, modules, vessels, piping, and auxiliary equipment is 98 bars/9.8 MPa [82], and Table 3 shows the tensile strengths of the 3D printable materials currently available that are exceedingly well above the operating pressures of 70

bars/7 MPa suitable for modules. However, it remains uncertain whether creep deformation of 3D printed plastics could happen during prolonged RO operations.

2.1.4. Resolution

The resolution of 3D printed spacers, modules, and other membranes will depend on the selected 3D printing technology. Tan et al. [106] found that MJM and SLS 3D printing provided more accurate parts than FDM, and that the surface roughness of the parts played a role in affecting the critical flux. Given that FDM has been more commonly associated with the printing of mechanically sturdy parts [69], future studies could examine the combination of mechanical durability for FDM layers with the high accuracy of SLA, SLS, DLP, and MJM printing technologies. The low resolution of FDM printers expands opportunities for the design and development for optimised membrane modules, however, the multi-material capabilities of 3D printers have not been fully utilised [34], limiting the current understanding of composite membrane modules that are yet to be further explored. Because of this compatibility from a low-cost and resolution perspective, there is significant potential for further membrane module optimisation studies utilising low-resolution FDM printers that will cut fabrication time and costs during experiments and allow for simulations using CFD analysis (Fig. 6). This module optimisation could potentially lead to lower energy consumption, lower fouling, and chemical usage [34]. While at higher resolutions the functional properties of the membrane can be experimented both at the spacer and layer level. Depending on the 3D printing technology used, laser spot sizes for SLA and 2PP, pixel sizes of liquid crystal display screens for DLP, or nozzle diameter for FDM, determine the resolution of the final printed part. These processes rely on the use of either UV-curing or heated material deposition to create the final model. However, resolutions required for the fabrication of nanoscale membrane features and at scale still remains a barrier to 3D printing. Additionally, post-processing processes such as acetone finishing can be used to improve surface finishes on parts [107,108], providing an aesthetically smoother visual should the poor resolution of the final model be undesirable.

2.1.5. Hydrophobicity and hydrophilicity of 3D printing membranes

Nearly all 3D printed photopolymer resins exhibit hydrophobic properties [109]. Recent 3D printing technologies have allowed designers to impart and design in hydrophobicity and superhydrophobicity onto printed objects. Despite this, 3D printed resins typically produce parts with high surface energy, requiring a second layer of coating that reduces this surface energy to make it more hydrophilic depending on the application. For MD, hydrophobicity is desired over hydrophilicity. While for FO and RO hydrophilicity is preferred. This allows a versatile

 Table 3

 Mechanical tensile properties of the 3D printing polymeric materials compared with commonly used materials within the desalination industry.

Material	Tensile strength (MPa)	Young's modulus (GPa)	Membrane manufacturing application	Remarks	Source
Acrylonitrile butadiene styrene (ABS)	37	2.32	AM, FDM	Rigid, impact resistant, insulating, abrasion resistant, good dimensional stability and definition.	[83]
Anycubic Plant-based UV Resin	36–52	-	AM, DLP	Biodegradable and zero harmful chemicals, and low shrinkage.	[84]
Anycubic Colored UV Resin 0.5KG	23.4	_	AM, DLP	Rigid and tough, ideal storage conditions between -35 °C to 15 °C, lower tensile strength, and shelf life of 18 months.	[85]
Asiga Dental PlasGray	51.1	1.9	AM, DLP	High thermal resistance, dimensionally accurate, and tough.	[86]
Asiga PlasClear	52.6	1.915	AM, DLP	Clear material, thermally resistant to 83 °C, and tough.	[87]
Cellulose Acetate	12–110	1.0-4.0	Conventional	Hydrophilic, good mechanical strength and chlorine resistance.	[88]
Ethylene glycol phenyl ether acrylate + 2-benzyl-2 (dimethylamino)-4'-morpholinobutyrophenone (crosslinker)	0.6-31 MPa	-	AM, DLP-SLA	Stiffness and dimensional accuracy increase with the amount of cross-linking.	[89]
Formlabs BioMed Amber	73 (cured)	2.9	AM, SLA	Higher impact resistance. Low thermal resistance. Expands under heat.	[90]
Formlabs Ceramic	5.1	1	AM, SLA	High thermal resistance, dimensionally stable, brittle, lower mechanical strength.	[90]
Formlabs FLPRGR01	35	1.4	AM, SLA	High precision, moderate elongation, and resistance to deformation.	[90]
Formlabs Standard Resin	38 (uncured) 65 (cured)	1.6 (uncured) 2.8 (cured)	AM, SLA	Good dimensional accuracy, robust, and smooth surface. Low thermal resistance, 60 min curing time, lower impact resistance.	[90]
Formlabs: High Temp Resin	20.9 (uncured) 58.3 (post- cured)	0.75 (uncured) 2.75 (post-cured)	AM, SLA	Heat deflection temperature of up to 238 °C at 0.45 MPa. High dimensional accuracy and thermal resistance.	[90]
Inconel	940	220	AM, SLS	High corrosion, oxidation, and thermal	
IP-G	-	3.4	AM, 2PP	resistance. Cryogenic environments applicable. High temperature resistance, printed at the nanometre scale, high speed fabrication of mesoscale structures.	[91]
IP-S	-	4.6	AM, 2PP	Smooth surfaces at the micro- and mesoscale, high accuracy and thermal resistance.	[91]
Nylon 12 Powder	50		AM, SLS	High toughness and thermal resistance, biocompatible and sterilisable.	[92]
PA 2210 FR	46	2.5	AM, SLS	Flame resistant, halogen-free polyamide, good long-term stability and chemical resistance.	[93]
Phrozen ABS-like Resin	12	-	AM, DLP	High hardness, moderate toughness and resolution. Tensile strength suited for industrial applications.	[94]
Phrozen Aqua-Gray 4K Resin	2	-	AM, DLP	Low tensile strength, hydrophilic (WCA = 35°), dimensionally stable and accurate, high toughness.	[95]
Phrozen Rock-Black Stiff Resin	30	-	AM, DLP	Sturdy, flexible models with a heat resistance of up to 97 °C. High tensile strengths with industrial applications.	[96]
Poly(vinylidene fluoride)	42.8	1.0-2.3	Conventional	High mechanical strength and toughness. Resistant to abrasion, creep, chemical degradation, and flammability. Is chemically inert.	[97]
Polyacrylonitrile	2.4-4.5	0.1352-0.2035	Conventional	High strength, chemically resistant, UV-resistant, heat resistant in fiber form.	[98]
Polyamide	50–100	1.5–3.3	Conventional	Nanometre pore sizes, high mechanical strength and thermal stability can be fabricated to nanometre thicknesses.	[88]
Polyamide-12	48–57	3.5–4.4	AM, MJM	Could be printed to good water tightness, strengths, and dimensional accuracies.	[99]
Polyetherimide (PEI)	32–43 (printed 30–45° resp.)	-	AM, FDM	High strength and rigidity, good long-term heat resistance, creep resistant, good electrical	[100]
Polyethersulfone	85	2.4	Conventional	properties, and good dimensional accuracy. High resistance to heat, impacts, acids and bases. Is hydrolytically stable against hot water	[101]
Poly-lactic acid (PLA)	50.84–57.16	-	AM, FDM	and steam. Good electrical properties. Bioplastic and biodegradable, low thermal resistance and malleable under high heat, low	[74]
Polypropylene	21.4	0.907	AM, SLS	mechanical strength, can be reused. Tough, fatigue-resistant, functional applications, for components,	[93]
Polypropylene (atactic)	21.4	0.689–1.52		-ppression, for components,	[88]

(continued on next page)

Table 3 (continued)

Material	Tensile strength (MPa)	Young's modulus (GPa)	Membrane manufacturing application	Remarks	Source
			Conventional and AM, FDM	Hydrophilic, high melting temperature, chemically resistant, and good mechanical strength. Used in MF to NF membranes.	
Polysulfone	70.3	2.48	Conventional	Tough, rigid, high strength, oxidative resistant, and good thermal and chemical stability.	[102]
Polytetrafluoroethylene	14	0.3	Conventional	Extreme thermal resistance and electrical insulation properties, low friction, and chemically resistant.	[103]
Projet Visijet M3 Navy	20.5	0.735	AM, MJM	Durable, high definition, low tensile strength and thermal resistance.	[104]
Projet Visijet M3-X	49	2.168	AM, MJM	High temperature resistance, good mechanical strength.	[104]
PVC	7–27	2.1–2.7	Conventional	Weather resistant, chemically resistant, corrosion resistant, shock and abrasion resistant. Used in pipes and insulating material.	[88]
Stratasys Dental Clear Biocompatible MED610/620	50–65	2–3.3	AM, Polyjet	High dimensional accuracy, tough, high hardness and durable. Low thermal stability.	[105]
Ultrasint PA6 MF Polyamide	62 (XY direction) 40 (Z direction)	3.3 (XY direction) 40 (Z direction)	AM, SLS	Mineral-filled, high ensile strength, stiff, good thermal and chemical resistance,	[93]

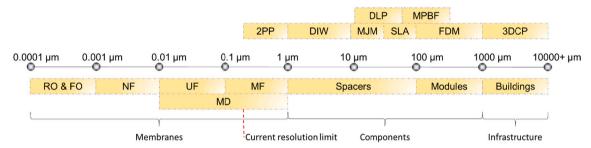
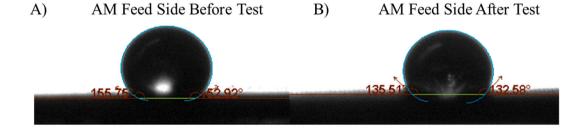


Fig. 6. Lower resolution printing confined to components and infrastructure fabrication for desalination plants. While printing limits become more visible for direct membrane fabrication (modified from [34]).



C) AM Permeate Side Before Test D) AM Permeate Side After Test

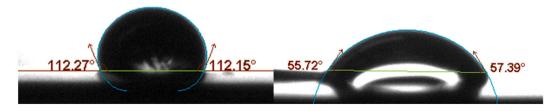


Fig. 7. The hydrophobicity of the MakeX PRO25 and PRO30 printer exhibited superhydrophobic properties on one side of the membrane (a) and hydrophobicity on the other (c), while after the test the membrane on the permeate side lost hydrophobicity (b) and more considerably for (d).

fabrication of membranes that can achieve both hydrophobic and hydrophilic properties, however, the low surface energy coating can also cover the nano features of the 3D printed membrane and potentially render it less effective [110]. Unlike MD where the membrane interface with the solutions is the important separating factor in allowing only water vapor through, liquid-phase water passes through FO and RO membranes, requiring the entire structure of the membrane to be hydrophilic rather than just the surface coating. Seen in Fig. 7, a partial explanation for this phenomenon is the presence of the smoother side of the membrane when peeled off the supporting plate of the DLP printer. While the rougher side (the side that is last exposed to the LCD UV light) has sub-micron pixel-cured rough features that make it more hydrophobic than the base side. Jafari's et al. [110] study provides suggestions in designing in circular protrusions which reduces the surface hydrophilicity of the membrane even if the part is hydrophilic in nature. By printing complex surface features at the sub-micron level, the hydrophobicity of the part will be enhanced even if the material is hydrophilic - greatly expanding the selection of materials to be used for MD. While for RO and FO applications, the hydrophobic nature of photopolymer resins makes it difficult to produce high-performing membranes unless the material is inherently hydrophilic. Therefore, hydrophobic polymers should be used for MD while for RO and FO hydrophilic polymers should be applied, which is the most significant challenge to current 3D printing processes to date for FO and RO. It is anticipated that the resolution, areas of the materials, and the build speed will improve [34,37].

Recent advances in 3D printing have expanded its applications towards producing both hydrophilic and hydrophobic resins. In one study, the addition of acrylic acid to the resin mixture poly(ethylene glycol) diacrylate turned the photopolymer superhydrophilic by lowering the wetting contact angle down to 0°, and superhydrophobic using 1H, 1H, 2H, 2H-perfluorodecyl acrylate [111]. These hydrophilic and hydrophobic additives allow tailored solutions to be made that expands applications towards all areas of membrane desalination. Additionally, both superhydrophobic and superhydrophilic materials can be printed on top of one another using PµSL 3D printing for microfluidics with potential applications for oil-water emulsion [111]. With high resolutions and multi-material opportunities, it is possible to directly fabricate membranes and desalination components with hybrid superhydrophobic-superhydrophilic properties, although this area of research has yet to be explored. A major possible barrier could lie in the long-term bonding strength between 3D printed superhydrophobic and superhydrophilic materials when fabricating membrane components with completely dissimilar surface energies, therefore, covalent bonding between dissimilar surface functional groups become a barrier to its high performance.

2.1.6. Chemical stability

The first instance of 3D printed membranes with some degree of chlorine resistance was done by Chowdhury et al. [112], where the electrospraying technique was applied to deposit droplets of trimesoyl chloride (TMC) and m-phenylene diamine (MDP) to react and form polyamide onto the surface of a charged role. The chlorine resistance of polyamide is on the order of between 200 and 1000 ppm [113]. While there is no clear definition of chlorine-resistance for membrane desalination [114], membranes can still suffer from degradation and perform either better or worse as a result. Imparting chemical stability can be achieved through surface coatings [115] and chemical modifications [116-118]. Possibilities for enhanced chemical resistance and stability of membrane can come in the form of chemical surface modifications and the selection of appropriate materials [58,119]. Ceramic 3D printing is one example of selecting a material that is inherently chemically resistant, where Ray et al. [58] 3D printed ceramic membranes, however, were brittle and would not be ideal for rolled designs and are more expensive than polymers.

It was hinted that certain plastics create leachates that are environmentally detrimental to marine life [120,121]. Therefore, the chemical

stability of a 3D printed membrane and its components cannot come at the cost of polymer leaching into the drinking water supply or environment through hydrolysis or unwanted reactions. FDM using ABS plastics at higher melting temperatures emit higher toxic particulates than PLA that affect respiratory function largely from the printing process [122]. Certain bio-printable plastics, considered safe by the industry, induced developmental toxicity within cell growth and embryos, requiring mitigation through post-processing steps to nullify the dangers [123]. On the other hand, PLA plastic is safe to humans due to its widespread use in food packaging [124], and may be the most appropriate material of choice for developing biodegradable, chemically stable components for desalination plants. Chemically stable components require strong chlorine resistance and non-existent leaching of toxic chemicals into drinking water supplies.

As fouling continues to be an issue for membrane desalination, 3D printing membranes and spacers must be chemically resistant to cleaning agents such as chlorine. Leakage of toxic materials into the drinking water supply is another cause for concern and fortunately enough, many of the polymers in use by the 3D printing industry can be safely consumed given its widespread use in the medical and dentistry industry. Because of the inherent limitations on the selection of 3D printer materials, the chemical resistance and toxicity of 3D printing components and membranes specific to desalination still requires further areas of research.

2.1.7. Mechanical stability

Submerging 3D printed polymers in aquatic saline environments can lead to deformities and deterioration in the structural integrity of the printed components. Ayrilmis et al. [76] investigated the properties of FDM printed PLA/Wood composite materials to thickness layers of 0.05 mm to 0.3 mm. PLA/wood composites were submerged for 28 days at 20 °C to detect for any swelling. Swelling was more severe with larger printing thicknesses due to water seepage into the pores of the material. Larger thicknesses led to higher porosities, leading to higher water absorption. Within desalination applications, this could create ripe conditions for bacteria and algae to grow within these pores, particularly for spacer fabrication that can contribute to greater biofouling. More undesirably, when fabricating modules that need to be watertight, deterioration in the structural integrity of the module may happen with time leading to fluid leakage. However, mechanical stability of 3D printed parts can be achieved through post-processing methods such as the application of acrylic-based varnishes that reduce porosities [78]. Mechanical stability issues are less likely to transpire in 3D printing technologies utilising lower layer thicknesses and porosities seen in SLA, 2PP, and DLP technologies where layer thicknesses of less than 50 μm can be achieved. Consequently, the disadvantage of reducing layer thicknesses and porosities is higher material-consumption and longer print times, which conversely and advantageously leads to much more sturdier models.

2.1.8. Industrial scalability

With the design and optimisation of new and innovative membrane spacers and modules, the next issue becomes apparent when the mass production of components for the water desalination industry is demanded. Currently, even with the commercial availability of 3D printers and its trend in the drop in prices since the late 1980s and early 1990s, the productivity and speed to which membranes could be fabricated using 3D printers is still low due to the additive layer-by-layer process. The cheapest and lowest resolution 3D printer in this current day operates off DLP technology, has a resolution of 35 μm , a print speed of 80 mm/h, a build volume of $132\times74\times130$ mm and has a cost of \$409 [125]. With large membrane areas on the order of 20 m² per module in some cases, the scalability for 3D printing technology is farfetched compared with other methods such as phase inversion and interfacial polymerisation. Currently, it is more economical to 3D print larger, lower resolution components for desalination such as modules

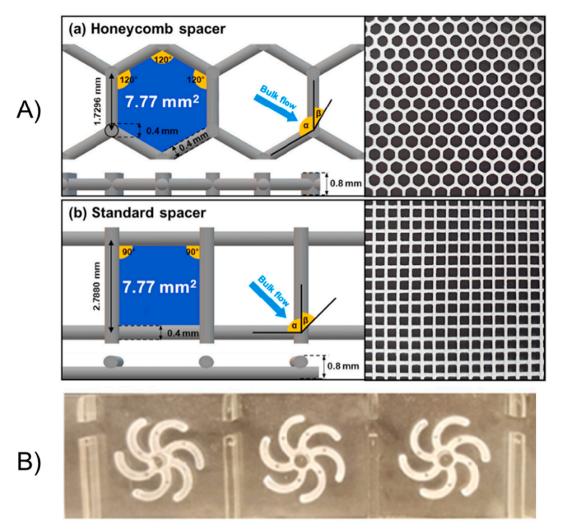


Fig. 8. (a) Honeycomb spacers to reduce fouling and improve flux [26], (b) turbopromoters reducing scaling and cake layer formations [50]. Reprinted with permission.

and spacers than it is for membranes. 3D printing is currently limited to producing small quantities of complex components. Another major issue with 3D printing is repeatability at the nanoscale. Even with pixel- and spot-based printing processes, 3D printing repeating nanofeatures at commercial scale is a challenge and even more so when examining for defects due to the myriad of factors that can affect the dimensional accuracy of the nanofabricated part such as vibrations and curing irregularities from the resin. The challenge here is the development of 3D printers that can fabricate large but highly detailed components at the micrometre and nanometre scale in large quantities. The recent release of the Uniontech RSPro 2100 SLA printer in 2020, the world's largest 3D SLA printer to date, has a build volume 2100 \times 700 \times 800 mm and a laser spot size of between 100 and 850 µm [126]. Using this setup, 2.1 m by 0.7 m spacers and multiple modules could be made. Compared with the Stratasys SLA-500 printer released in the 1990s, the build volume is 508 mm \times 508 mm \times 610 mm [127]. An approximate increase in 1 m³ was achieved over the three decades for SLA. Meanwhile, much larger 3D printing technologies can build volumes as big as 10 m³ which can print car-sized models [128]. FDM printers will less likely encounter scalability issues compared with other finer resolution, laser-based printers where build volumes are determined by the space allowed for a moving extruder. Scaling up 3D printing continues to be a major challenge, and this is likely to be more arduous for UV- and laser-based printers compared with thermal extrusion technology.

3. Future perspectives for 3D printing applications for water desalination

Tijing et al. [35] suggested future investigations into the use of combining 3D printing with other traditional membrane and manufacturing processes, and the forthcoming advent of 4D printing where 3D printed features change properties and performances in its operating environments over time (such as twisting, curling, and bending, and folding designs). The combination of traditional membrane fabrication methods such as electrospinning with 3D printers, hybrid manufacturing with subtractive and formative manufacturing approaches, and 4D printing – where 3D printed objects can adapt and change with time in the environment, with an example being rotating spiral spacers [54], were proposed. However, these perspectives do not address the material and resolution limitations for the 3D printing fabrication of membranes.

Previous 3D printing applications for membrane desalination included the use of TPMS spacers with improved scaling-resistant properties as salinity concentrations increase with time [24,28,29,49] reflecting the advantages of 4D printing, and feed spacers with turbulence-promoting parts [50]. 3D printing for membrane desalination opens avenues to explore new designs and its behaviours when submerged in aquatic environments.

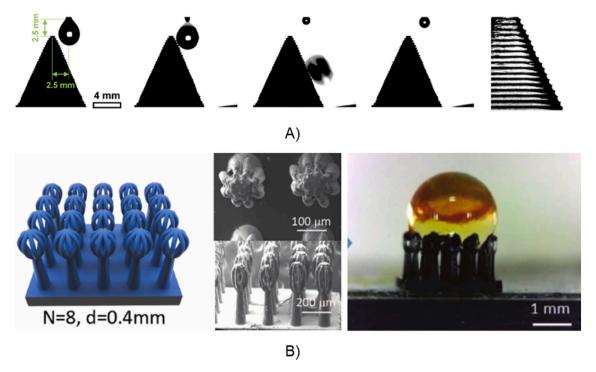


Fig. 9. Images showing the hydrophobic properties of 3D printed surfaces applicable to water treatment and desalination (a) FDM 3D printed micro-pyramids showing hydrophobic patterns and performance [129], (b) 3D printed microstructures mimicking the superhydrophobic properties of the *S. molesta* leaf [130]. Reprinted with permission.

3.1. Membranes

3.1.1. Modified feed spacers for anti-fouling and flux enhancement
Currently, commercialised direct fabrication of membranes for water
desalination is not yet achievable, while for lower resolutions larger

components of membrane desalination systems such as spacers can be designed and fabricated using 3D printing technologies such as SLS, DLP, and SLA [21,24,56] for enhanced filtration. There are inherent limitations in the use of conventional spacers due to the lack of turbulence promoting characteristics that help mitigate the onset of fouling

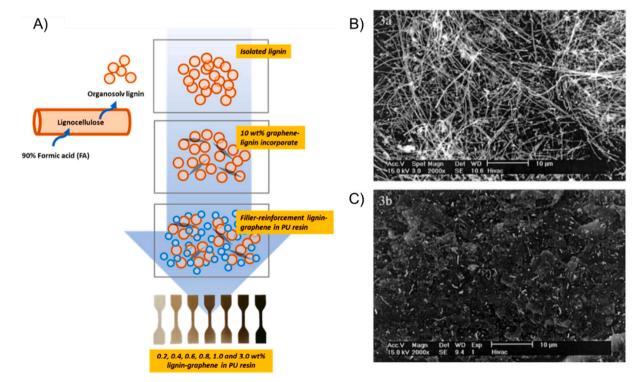


Fig. 10. (a) DLP printing with organosolv lignin fibres was used as reinforcement material with graphene nanoplatelets, improving tensile strengths by 27%, reprinted with permission [81]. (b) FDM fibres before printing that shows a lack of structure and (c) after printing, showing a clearer structure, reprinted with permission from [132].

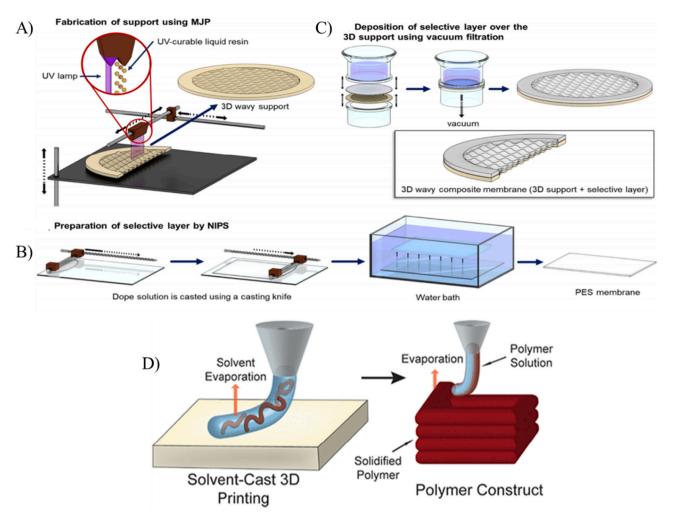


Fig. 11. 3D printed wavy composite membranes with anti-fouling properties: (a) the printing of the support layer, (b) PES casting of the selective layer, and (c) vacuum process to adhere the two support and selective layers together. (a–c) Reprinted with permission from [142], (d) solvent embedded with a polymer allowing for the evaporation to create a thin film on membrane surfaces, reprinted with permission from [143].

and scaling on membranes.

The incorporation of new and innovative spacers for fouling mitigation has been very promising and can be seen in the studies shown in Table 2 and Fig. 8. The increase in turbulence prevents the adhesion of foulants to the surface of membranes while promoting flux in the process. Therefore, the focus of flux is shifted away from surface coatings on membranes to turbulence-induction using spacers. In addition, promoting turbulence using spacers has an additional advantage of reducing the concentration polarisation at the surface of membranes [24] and reducing reverse solute flux in FO [53]. Conventional feed spacer has some limitations in creating flow unsteadiness in the membrane channel that results in increased fouling and lower flux. It has been presented in many studies that modifying the geometries of the feed spacers can increase the turbulence. But the modified feed spacers with complex geometries are difficult to produce using conventional techniques. However, 3D printing technology can be used to fabricate these spacers to enhance the filtration performance.

3.1.2. Designing superhydrophobic membrane surfaces

Mechanical features and patterns to increase the roughness of membranes can be designed into the surface at the sub-micron level without the need for further surface chemical coatings and modifications. This represents a paradigm shift away from employing chemicals with inherent hydrophobic properties that prevent wetting, limit fouling, and improve fluxes. Kang et al. [129] developed a hydrophobic surface with a contact angle of ${\sim}143~^{\circ}C$ and a surface roughness of 36.42 ${\mu}m$ (Fig. 9). The surface demonstrated a rolling-off phenomenon, supporting the use of current 3D printing technologies for future scaled production of hydrophobic components. The design and fabrication of 3D printed superhydrophobic surfaces into membranes could lead to reduced biofouling for membrane distillation processes, leading to prolonged flux improvements and lower performance decline with time. Different superhydrophobic features could be designed into the membrane's surface that can lead to highly optimal and beneficial properties. By altering these features, membrane designers can experiment and develop membranes with the right properties for commercial applications.

3.1.3. 3D printing nanofiber reinforced and composite membranes

The successful commercialisation of TFC membranes in the past could see a renewed path utilising 3D printing for composite membrane desalination. The combined use of different materials each serves a unique purpose in TFC membranes. With an active barrier layer to prevent the passageway for salt ions, a porous layer, and a support layer to improve membrane mechanical durability. Given a wide range of materials ranging from ceramics, polymers, metallics, and other composites have been used to fabricate models, its applications towards membrane manufacturing should not be overlooked. The benefits of multi-material printing of nanofibrous and composite materials were realised in past studies [77,80,131–133] where higher tensile strengths

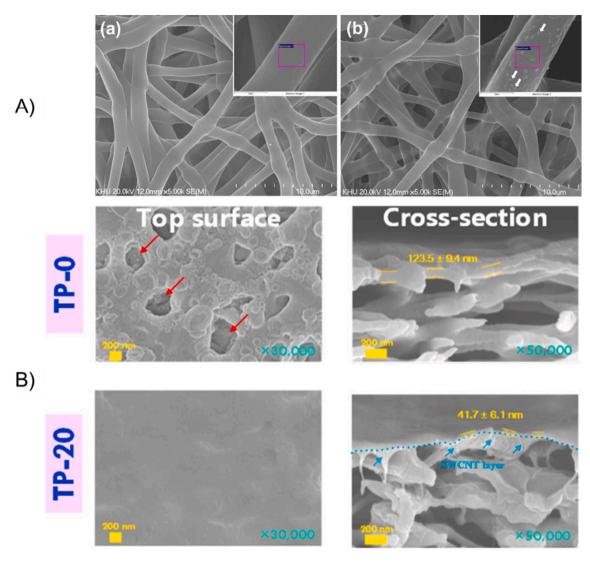


Fig. 12. (a) Embedded silver nanoparticles inhibited the growth of pathogens and water borne diseases [136], (b) polyamide active layer and pore sizes were both reduced from single-walled carbon nanotube coatings [145]. Reprinted with permission.

and hardness were found through composite 3D printing materials. The proper mixing of this material was just as, if not, more important as the printing conditions itself. Ensuring that uniform properties of the material would allow printed components not to fail due to the presence of unwanted voids. Fibres could be printed within membranes that would improve its mechanical strength using both DLP and FDM technologies (Fig. 10) that are crucial properties for high-pressure RO applications. Rather than printing supporting layers, fibrous supporting matrixes could be embedded within the membranes, further reducing the overall thickness, and improving the manufacturing times by printing both supporting fibres and the membrane material in one go. To date, multimaterial printing has been used in the areas of FDM-PLA [134], DLP-SLA [89] and inkjet [135–137] printing. By combining multiple materials within 3D printing, membrane compatibility [138], versatility [139], and durability [89] could all be improved, making 3D printed membranes highly applicable and appropriate for more commercial desali-

In the manufacturing of conventional membranes seen in symmetric, asymmetric, and composite TFC membranes, 3D printers can currently fabricate models consisting of more than one material for metals [140] and polymers [141]. With asymmetric and composite membranes consisting of a dense, porous, selective, and mechanical support layer, 3D printers can use multiple nozzle heads or resins to print different layers

of distinct material for a single model. Mazinani et al. [142] and Al-Shimmery et al. [57] 3D printed a support layer which was then superimposed with a selective layer, creating a wavy featured membrane which exhibited anti-fouling benefits and improved water permeability (Fig. 11(a-c)). The issue with this design is the lack of rollability, which is standard to that of RO desalination plant modules. The use of low-resolution 3D printers to fabricate support layers is currently feasible, however, there lies the limitation of scaling up the entire process and developing high resolution printing materials that can endure 3- to 5-year operating conditions found in RO desalination processes. Thin film layers have also been experimented with the use of PLA plastic suspended within a solvent which will later evaporate to leave a film, known as solvent-cast printing (Fig. 11(d)) [143]. The advantage of solvent-cast printing is that high resolutions can be achieved and expands the range of polymers usable for 3D printing. However, solvent-cast printing is a recent development and further studies into understanding the fluid drop mechanics, moderation of the evaporation process, development of rapidly solidifying solvents, and creation of dedicated composite thin film systems are all needed. It becomes possible to print symmetric, asymmetric, and composite membranes using these 3D printing technologies in the foreseeable future.

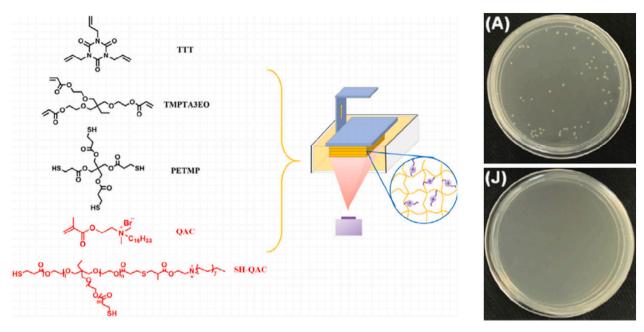


Fig. 13. DLP 3D printed quaternary ammonium salt with methacrylate used to eliminate microbial growth from the surface of the photopolymer resin, with (A) showing *Escherichia coli* with no quaternary ammonium salt-type antibacterial agents. While (J) shows no bacterial growth after inoculating the 3D printing resin with 8% concentration of the antibacterial agent. Reprinted with permission from [153].

3.1.4. Nanoparticles for 3D printed surface coatings and embedding

Using inkjet printing, Ngo and Chun [144] produced surface coatings with superhydrophobic properties using regular laser printers. While office printers are a mature and well-established technology, its applications through membrane modifications towards water treatment and desalination has been recent, particularly in the use of nanoparticles and materials such as graphene oxide, silver (Ag) (Fig. 12(a)), and carbon nanotubes (Fig. 12(b)) [135–137,145]. Embedding nanoparticles within

3D printer materials enhances properties that would otherwise not be possible when used purely on its own. With this application, the uniform distribution of nanoparticles within the 3D printed polymers for membrane fabrication is an area of promising application that removes the additional procedures taken for uniform distribution within membrane active layers. Pawar et al. [146] reduced the curing times and prevented the need for harmful solvents by using 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide as the nanoparticle additive to the UV-curable inkjet

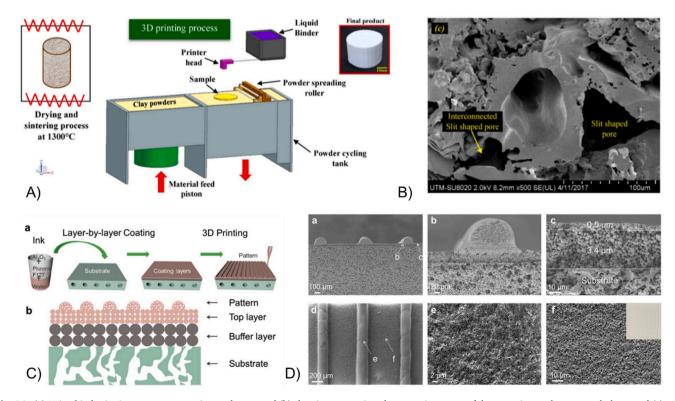


Fig. 14. (a) Using binder jetting to create ceramic membranes and (b) showing a scanning electron microscopy of the ceramic membrane morphology, and (c) using ceramic inkjet printing and (d) with the same membrane morphology. Reprinted with permission (a–b) [167] and (c–d) [160].

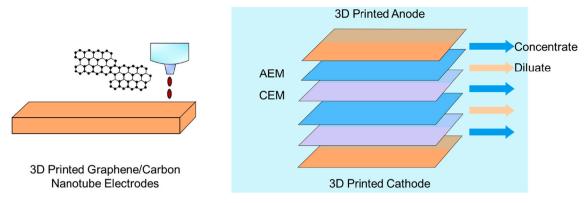


Fig. 15. 3D printing applied to the fabrication of highly durable electrodes for salinity gradient power generation in RO plants.

solution. The environmental impacts in the form of reduced harmful chemical usage and faster curing times (translating to lower energy consumption) were achieved through this technology. Similarly, for membranes and membrane components fabrication, the benefits could be realised when nanoparticle additives can speed up production times and improve other properties without further post-treatment. Addition of nanofillers enhanced the mechanical strength of 3D printed parts for another study using FDM printing, with the tensile and flexural strengths respectively improving by 25.7% and 17.1% [147] with similar compressive strength improvements observed for ceramic materials [148]. Therefore, a range of factors can be affected such as the membrane's permeability, selectivity, hydrophobicity, hydrophilicity, conductivity, mechanical strength, thermal stability, and anti-microbial properties [149] when utilising nanoparticles and nanofibers in the development of membranes for water treatment and desalination. Though, its uses in water treatment and highly septic environments teaming with microbial activity might see more suitable applications where biofouling poses a more severe problem compared to that of seawater. Depending on the type of water treatment technology, the materials of nanoparticles used should be compatible with and be used to improve the performance characteristics of the membrane. For example, the imparting of hydrophilic nanoparticles for FO and RO membrane, and hydrophobic nanoparticles for MD. The bondage between the nanoparticles and the polymeric medium should also be strong enough such that these particles do not leak out into the solutions as previous studies have observed [150,151], while its introduction may induce undesirable characteristics including lower thermal stability [152].

3.1.5. 3D printed biofouling resilient membranes

3D printing can accommodate a range of materials with properties that resist the growth of bacteria and viruses on the surface of the part. Currently, DLP printing technologies have explored the use of mixed matrix resins with anti-microbial properties [153,154]. With DLP 3D printing, membranes fabricated with antimicrobial properties with this technology could have the potential of outperforming existing membranes with antimicrobial TFCs (Fig. 13). The antibacterial rate for these resins was shown to be 100% [153] compared with other works in membrane literature that showed an antibacterial effectiveness of around ~80% [155-157]. Therefore, future developments in antimicrobial 3D printed membranes might pave way for membranes with highly effective antifouling properties, however, the issue of scaling may present itself as an entirely separate problem. Because of this inherent antimicrobial nature of the membranes, the addition of pre-treatment chemicals within the water supply may not be necessary in some cases, saving further operating expenditure costs on chemical purchases and consumption and preventing membranes from degrading due to the exposure of harsh solutions and reagents.

3.1.6. Ceramic 3D printed membranes for pretreatment systems

Currently, it is possible to 3D print microfiltration (MF) [158,159] and ultrafiltration (UF) [58,160] membranes to enhance flux performance. SLS printed polymeric microfiltration membranes have been fabricated which provide opportunities to adjust rejection rates and fluxes by changing polymeric particle sizes and distributions [158]. Likewise, these MF membranes have achieved rejection rates greater than 90% [158,159]. Meanwhile, ceramic materials can be fabricated for MF, and it is also used for membranes requiring smaller pore sizes for ultrafiltration pretreatment. The use of Solvent based Slurry Stereolithography (3S) 3D printing methods can also be applied to fabricate ceramic membranes. The key advantages of developing ceramic membranes are its chemical inertness, designability for antifouling features, mechanical strength, lower pollution on the environment, higher filtration fluxes, stronger thermal resistance, longer membrane life, and better backwashing cleaning operations using high-pressure water [161–164]. The advantages of using ceramic as a filler is its cheap cost, where ceramic materials like clay, kaolin, and fly ash could be printed cheaply and quickly - costing as little as between \$0.07/kg to \$1/kg [165–167] with the added benefit of rapid prototyping complex structures ranging from a few minutes to hours [36]. As opposed to 3D printing with polymers where the porosity of the plastics is nearly zero and that pores or holes must be directly printed, the porosities generated by the voids between the powder particles are what define the pore sizes within ceramic membranes. Therefore, adjustments to the powder particle sizes, such as by grind milling, can be done to modify pore sizes and the porosity of the membrane. The rise in the adoption of ceramic 3D printed membranes will increase the compatible availability of chemicals used for pretreatment desalination plants, potentially reduce ongoing costs of membrane replacements due to high backwashing efficiencies and longer membrane lifespans, and lead to greater overall prolonged reduction in membrane fouling and scaling. However, the high costs are more likely to come from the time it takes to sinter the membranes, and the energy consumed during the sintering process, which can all be mitigated through manufacturing at an economy of scale. Fig. 14 shows the various works that have experimented the use of 3D printing for ceramic membranes.

3.1.7. 3D printed electrodes for brackish water and post-treatment desalination using membrane capacitive deionization

Recent advances in 3D printing have been applied to the fabrication of electrodes using nitrogen-doped graphene oxide/carbon nanotubes (GO/CNT) as the material [168]. This led to electrodes with more cycle times and higher durability, salt removal capacities of 75 mg/g, and improved energy recoveries of up to 27% [168]. Membrane capacitive deionization using metal oxide CNTs has been experimented where salt removal capacities was 6.5 mg/g with an efficiency of 86% was reached in salt removal capacity [169]. Combined with the fact that CNT fibres can be made continuously, the scalability of 3D printed CNT electrodes

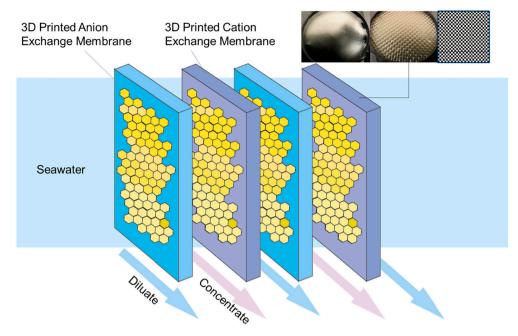


Fig. 16. 3D printed pattern exchange electrodialysis membranes for desalination. Adapted from [185].

provides enormous opportunities for industrial applications in the RO desalination industry. The improved energy recovery rates and the longevity of 3D printed electrodes would reduce the energy consumption of the overall RO plant when fed back into the system, and lower electrode replacement costs and frequencies. Therefore, this setup (Fig. 15) addresses the significant barrier that RO plants currently face its high energy intensity. Similarly, other studies have used graphene combined with CNTs as electrode material [170-173], where these studies have reported improved: strengths, electrical resistances, longevity, porosities, and power generation performance for the electrodes. 3D printed GO/CNTs could promise better performances compared to conventional electrodes from using various free-standing 3D printed structures that could drastically improve desalination performances. Its applications in water desalination are still currently in its early infancy stages. Currently, capacitive deionization has applications in post-treatment of industrial brine and zero liquid discharge systems [174], bromide removal [175,176], and selective removal of valuable metals and nutrients [177].

3.1.8. 3D printed electrodialysis exchange membranes for brine treatment and water recovery

The use of electrodialysis (ED) technology to treat RO brine has been done in previous studies [178-184]. However, it was only recently that 3D printing technologies were used to fabricate membranes for electrodialysis [185,186]. Seo et al. fabricated patterned exchange membranes for electrodialysis that showed lower ionic resistances, which holds the promising potential to improving the performance of ED membranes in the treatment of saline solutions particularly in energy recovery through harnessing salinity gradient power (Fig. 16). Limiting current densities have been improved by 21% through 3D printing of complex frames for improving the flow of ED streams, leading to improved desalination performances and lower costs [187]. When applied to the post-treatment of brine from RO plants, the possibilities for ED to improve water recoveries is immense, particularly with recent studies covering ED for RO zero liquid discharge systems [188-190]. Recoveries between 77% [189] to 85% [191] were achieved with brine salinities as high as 125 g/L being concentrated [189], while even higher concentrations from 70 to 245 g/L was attained with ED posttreatment brine concentration [192]. With the incorporation of 3D printed ED patterned membranes, better energy recovery percentages

and desalination performances could be realised given the potential for higher limiting current densities and lower ionic membrane resistances, with positive impacts on the environment where brine is no longer discharged into the ocean with the incorporation of 3D printed patterned post-treatment ED membranes for RO brine concentration and zero liquid discharge.

3.1.9. Surface functional groups

Some studies have examined surface functional properties for 3D printing plastic covalent bonding strengths via modifications. Several surface modifications methods to strengthen covalent bonding include alkaline surface hydrolysis, atom transfer polymerisation, photografting by UV light, plasma treatment, and chemical treatments after plasma treatment [193,194]. Various studies for example have used dopamine [195–197], alkaline hydrolysis [198], surface entrapment with chitosan [199] to modify surfaces for 3D printable plastics to serve as adherent platforms for post-modification with additional materials. These studies have shown successful bonding strengths between the chemicals after surface modification was completed. Surface modifications using metals have been shown to yield greater strengths [200] and fatigue endurances [201]. However, there are still challenges required for this to be realised, one being the study of sturdy and durable surface functional layers on a variety of different substrates [194] that are required to produce successful and commercially viable membranes through 3D printing. These studies show the possibilities for 3D printing materials to have an affinity towards successful surface modifications that will help make 3D printed membranes highly comparable to that of conventionally fabricated membranes. Currently, DIW printing is helping to achieve this.

3.2. 3D printing infrastructure for desalination plants

While 3D printing for membranes is confined at the micro scale, in applications where resolution is not an issue, the fabrication of structures through 3D printing onsite can help reduce the engineering and procurement costs (EPC) of desalination plants. This will significantly reduce the engineering and procurement costs by printing components onsite, therefore, reducing construction and logistical costs on the project. The advantages of applying 3D printing for construction were cited to reduce time and costs, improve the level of customisability,



Fig. 17. 3D printed water storage tank from Teslarati [210].

higher sustainability, reduce material consumption, and increase the safety of work [48,202-203]. In line with previous 3D printing works, the price of 3D printing infrastructure goes down the more recycled aggregate was used [64], however, the environmental impact is much larger than that of cast-in-situ concrete when raw unrecycled cement is used in the mix to maintain the strong foundations required [205]. The challenges for the use of 3D printing concrete structures are the right mix of plasticisers and silica, with too high of a viscosity leading to lower to no extrusion rates that could withstand high yield stresses [203]. The material mixture barriers and the significant environmental impact that 3D printing infrastructures can have is still a recent area for further investigation. While the benefits for greater customisation and recyclability of materials are obvious, the potential to significantly reduce the EPC of desalination plants should not be overlooked. Although the need for complex architectural designs is absent in desalination plants, the primary incentive for its application is the reduced costs and greater sustainability to produce all the required different assets.

3.2.1. Desalination buildings and water tanks

3D printing of buildings on desalination plant sites will lead to environmental and procurement cost savings. This is a new area of research that is currently still being studied with limitations confined to the selection of structurally sound materials. The main benefits for the 3D printing of buildings are the improved safety, cost reductions through improved construction methods such as "Contour Crafting" and D-Shaped printing, and reduced pollution on the environment [48,204,207]. The reduced labour and framework costs resulting from automated 3D printing of construction materials will be a strong focal point for interested desalination plant operators [206]. However, the use of concrete directly for 3D printing will have a higher negative environmental impact compared with conventional in-situ techniques [206]. In future applications of 3D printing for infrastructures, particularly for desalination plants, the selection of materials that are more sustainable and structurally sound is needed to make the technology more advantageous over conventional construction. Another main advantage is the construction of irregular building shapes, a benefit desalination plants will find irrelevant. However, irregular designs may see more practical use when desalination plants are located within harsh terrain. Currently, 3D printing for infrastructure is confined to small scale buildings as opposed to large-scale ones such as skyscrapers [207]. Because multi-story buildings are rarely ever used for desalination plants, this makes the technology highly compatible. Solutions such as pre-fabrication of buildings, changing designs as it is made, and optimising the infrastructure according to unique operating and design conditions, are some other benefits that 3DCP could have. Current

limitations include not being able to print overhanging structures, non-standardised concrete testing for mechanical strength, the need for reinforcement in some areas, and mechanical integrity [208]. Mesh reinforcing methods combined with 3D printing were applied to work around the issues of low mechanical strength for concrete structures by embedding steel rods for before and after printing [209]. Similarly, water storage tanks (Fig. 17) can also be fabricated alongside 3D printed buildings, producing all of the necessary infrastructure needs through one printing platform.

3.2.2. Pipelines

3D printing of pipes is an emerging field currently limited by its weak interlayer bonding strengths [211]. Zhang et al. [211] proposed printing according to the axial strengths being applied that would enhance the end product's mechanical strength. While path planning provides a greater degree of freedom to design pipes, they lack the mechanical strengths that are acceptable for high-pressure desalination processes. Other studies have used methods such as changing the print paths to enhance the pipe's surface quality [212–215]. Future 3D printed pipes will have both the freedom of producing entire pipelines that are also mechanically strong and versatile in design. Currently, some computer aided design (CAD) software can automatically generate pipes, which reduces time and cost on both production and design engineering tasks.

Meanwhile, recent advancements in 3D printing technologies make it possible to print sensors directly into pipelines during manufacturing [216]. This allows easy identification and monitoring of the pipe's conditions throughout the lifetime of the plant, while protecting the sensor from the harsh seaside environments – paving way for predictive maintenance solutions and the use of digital twins [217,218]. This means that pipes can be stored underground and monitored using this tagged sensor system, thereby reducing the overall footprint of the plant when land scarcity is an issue. Integrating temperature and salinity sensors within the pipelines could also be done using this technology, providing much more versatile options that would support the digitisation of desalination plants that are increasingly gaining attention due to the potential for reducing energy consumption [219,220]. Therefore, embedding sensors within pipelines allows for the complete integration of monitoring temperature and salinity conditions with digitised desalination plants, reducing footprints that can address issues regarding land scarcity and better energy efficiencies.

3.3. Components

3.3.1. 3D printing for optimised membrane modules

The advantages of using 3D printing are the ease of experimentation and optimisation of membrane modules for a wide variety of emerging desalination technologies such as reverse electrodialysis and MD. Currently the lack of module optimisations for MD [221–223] has driven the price of membrane modules for these studies. Meanwhile, another experiment has shown that the cost for membrane modules was a barrier [224]. This lack of standardisation and labour intensity to fabricate membranes is a barrier in the experimentation and optimisation for more effective emerging desalination systems.

For MD, thermal limitations and barriers must also be overcome, particularly in longer-termed studies where feed temperatures as high as $80-90\,^{\circ}\mathrm{C}$ are used which can lead to warpage and thermal creep within the printed modules. There are likely promising applications for 3D printing in the design and optimisation for FO modules, given that the cost of FO membranes is among the highest for FO and there is the absence of both thermal and hydraulic pressures involved. For example, Linares et al. [225] conducted a sensitivity test and showed that membrane modules contributed significantly to the FO plant costs.

Studies that have experimented with 3D printing to optimise performances using printed spacers and modules were made. Frames and innovative features were printed for AGMD modules in another which maximised the latent heat recovery from the solar-MD operation [225].

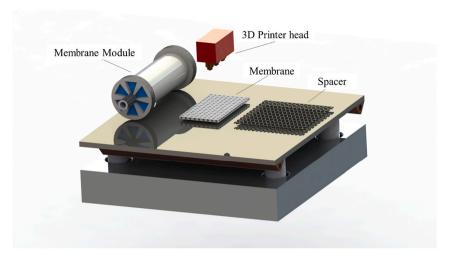


Fig. 18. 3D printing with the potential of fabricating all of the components in one go, resulting in cost savings through reduced logistics.

This was achieved by varying the thicknesses of the frames which provided the air gap, therefore improving the overall thermal efficiency of the solar-AGMD system. The use of complex models such as helical baffles, otherwise impossible for conventional fabrication, were used to recycle thermal energy, which reduced energy consumption by ~60%, and improved the compactness of the overall VMD design [226]. Therefore, 3D printing provides a myriad of opportunities towards improving the viability of MD systems by allowing complex and intricate designs to be fabricated beyond the conventions of subtractive manufacturing processes. Costs in experimenting with different parameters such as air gap widths, wall thicknesses, materials, and surface properties using 3D printing can greatly reduce the cost of research and development for MD systems. Currently, MD is an emerging desalination technology which can potentially have its commercialisation status expedited through greater adoption of 3D printing for unconventional MD module designs, fabrication, and experimentation.

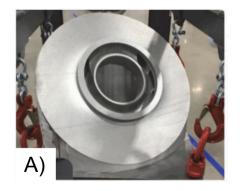
3.3.2. Complete 3D printing of membranes, modules, and spacers

It has been proposed that the fabrication of the entire membrane, spacer, and module all at the same time will further cut down costs [39]. While this has not been performed yet, printers are currently able to print with multiple materials, combining the fabrication of the entire pretreatment system with ceramics and polymers for flexible manufacturing of entire pretreatment cartridges. This simplifies the entire design and engineering process as opposed to traditional manufacturing processes where membrane, spacer, and module fabrications have been manufactured separately, requiring more complex logistical supply chains to deliver them to a central location for

assembly. The simplified complete printing of membranes, spacers, and modules is visualised in Fig. 18.

3.3.3. Metal 3D printing of heat pumps for MD energy recovery

For heat pumps, the use of SLS technologies to produce unconventionally complex metal shapes for highly efficient heat-transfer operations was also explored in other works [227-235]. Such uses could be applied in heat pumps for thermal extraction from permeate streams and thermal recycling in MD desalination. These improved thermal performances could also be used for MD thermal pumps in recovering latent heat from permeate streams. Thermal recovery reduces wasted thermal energy in MD setups and allows for the further reduction in energy costs and consumption. Given most MD systems utilise low-grade waste heat or renewable sources, the improved efficiencies lead to greater output for lower input. Likewise, the application for SLS metal printing technologies to MD heat recovery pumps remains yet to be studied and shows promising future applications in advancing the commercial viability for MD when complex heat sinks can be made to extract heat from permeate water. The combined use of SLS for both pumps and heat absorbers provides the benefits of improved thermal absorption from the permeate stream and thermal energy storage for prolonging the use of solar-based MD systems well into the night. However, future challenges for SLS printing for MD are the study of material properties in desalination settings given that SLS materials differ in properties against its bulk counterparts [236]. Further studies into SLS materials and its response within desalination environments are needed before fully appreciating the benefits SLS printing for heat sinks for MD heatrecovery pumps.



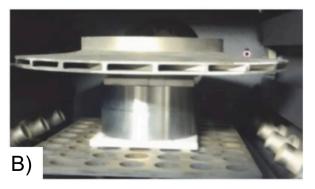


Fig. 19. Metal 3D printing with IN718 material taken from [249] through open access, (a) showing the final prototype of the metal impeller and (b) during the fabrication process Metal 3D printing of pumping components will reduce manufacturing costs and time, contribute to cheaper desalination plants, and improved maintenance, and operating life of pumps.

Table 4Recent applications of 3D printing towards additive manufacturing pump components.

3D printing technology	Pumping component	Remarks	Source
FDM	Impeller	FDM cost 40€ and 3 h, conventional fabrication cost is 150€ and 2 days. Post-treatment low-cost acetone soaking for improved surface finish.	[261]
FDM	Impellers	Slightly higher performance over conventional centrifugal pumps but used ABS as the material. 15% head loss reduction compared to cast iron impeller pump.	[262]
FDM and HM	Curved spacers for centrifugal pumps	3D printing of spacers led to 2.2 h manufacturing time using additive-3D printing (with conventional PLA), compared to 10 h for subtractive manufacturing-3D printing (with Stainless Steel 2205).	[263]
Sintering/ Laser Beam Deposition	Turbomachinery Impeller	Inconel 718 used. Pump material resistant to temperatures of up to 400 °C. Corrosion resistant to water, H ₂ S, and CO2, pressure resistant and high strength. Used Topological Optimisation software to design an optimal 3D printed pump simulated virtually.	[248]
Electron Beam Melting	Impellers and Plate	First time study fusing wrought plate by electron beam melting of an impeller onto it.	[264]
Direct Laser Metal Sintering	Impellers	Topological optimisation to produce 3D metal printed impellers with elevated performances using Inconel 718 as the material.	[265]
SLM	Impeller	Repairs conducted on centrifugal impellers using 3D scanning, digital reparations, and rapid additive metal manufacturing via SLM.	[266]
SLM	Impeller	Different internal lattice structures of impellers yielded better performance, with lattice impeller suffering 20.2% less deformation over solid—filled impellers and 10.7% better residual stress.	[267]

3.3.4. 3D printing for enhanced pump maintenance, performance, manufacturing, and durability

The use of polymers for 3D printing will see limited applications in membrane desalination due to low mechanical strengths tolerating pressures of up to 400 kPa [237], with many current applications confined to microfluidics [238–240]. Currently, limitations for 3D printing polymer-based pumps are the high surface roughness and low mechanical strengths, therefore, alternative non-polymer materials must be used for impellers and pumps. Wax patterns can be 3D printed and cast into metallic pumps which can then receive finishing operations to create a smoother surface [240]. Laser metal deposition (LMD) uses a high-powered laser to melt metallic powder which is carried by an inert gas [241]. Unlike other forms of 3D printing where printing is confined vertically as seen in SLS or selective laser melting (SLM), LMD can create parts in any direction and axis orientation [242,243] and can expedite the fabrication time of parts in any direction of geometry. The use of

various alloys combined with hybrid manufacturing also makes it possible to produce corrosion-resistant parts [243–246]. This corrosion resistance makes it possible for pumps to be used in environments with higher pH and salinity. Combined with hybrid manufacturing, pump refurbishment, and repair costs will also be reduced for these advanced pumps [247,248]. However, it is still currently unclear which alloys are the best used for the additive refurbishment process within pumps exposed to harsh environments, and further research is still needed in this area to better understand behaviours such as hydrolysis and corrosion reactions between 3D printed composite metallic alloys and seawater. One of the latest metals used in 3D printing for pumps - Inconel 718 (Fig. 19) – enabled researchers to explore optimal impeller designs for pumps which can also be applied towards developing highly efficient energy recovery devices.

Pumps within desalination plants will operate under harsh conditions, safeguarded by metallic alloys that are resistant to corrosion, maintained and easily repaired through combined technologies that scan, identify issues, rapidly printed components for installation, and with newer and more advanced pumps that are optimised for different desalination operating conditions and environments without expensive retooling.

Table 4 shows recent studies conducted on the use of additive manufacturing for metal and polymeric pumps, which yielded benefits in lower manufacturing times, lower costs, and a wider selection of materials that are corrosion and thermally resistant. Currently, compact pumps can have operating pressures rated up to 100 bar [249], while larger industrial versions could have maximum pressures of up to 300 to 345 bar [250,251]. Pumps operating with renewable power sources for smaller scale RO tend to be lower with operating pressures of around ~40–65 bar [252–255]. This will of course vary significantly depending on the abundance and reliability of renewable power. However, operating pressures are limited to the membrane mechanical strengths tolerable, the desired water recovery rates, and increases in the salinity concentration of the feedwater. As a rule of thumb, for every 1000 mg/L of salt concentration increase, an added 0.76 bar is applied to RO pumps [256]. For standard RO, this is between 50 and 70 bar [257,258]. For seawater intake pumps, this pressure is substantially lower, being between ~2 and 5 bar [259] [260]. Therefore, it is likely that seawater intake pumps will see firsthand applications of 3D printing in its parts fabrication and repairs due to lower operating pressures.

The freedom to customise and print new membranes using Inkjet printing shows the most promising outlook and solves the challenge confining 3D printers to the small range of materials that can be used for water desalination. The sub-micron resolutions that 3D printing provides allow for the design of hydrophobic surfaces on the surface of membranes, further enhanced with surface coatings that make membranes ideal for MD applications and having anti-fouling properties. While mass-customisation and optimisation of spacers and modules reduce the cost on membrane researchers to design and test unique module and spacers for the best setup in each of the desalination technologies, while allowing new and optimal components to function best by changing its design features depending on the operating conditions of the desalination plant. Lastly, while 3D printing has been synonymous with sub-micron resolutions and the production of custom small parts, at much larger resolutions, 3D printing can yield environmental and EPC advantages when designing and constructing entire desalination plants. Although components such as pipes and water storage tanks are standard components and the printing of modules able to withstand high pressures is far off, custom buildings particularly in difficult to reach regions may benefit from the use of 3D printing for infrastructure printing.

3D printing is still an emerging state of technology despite its origins tracing back to the mid-1980s. According to Gartner's hype cycle examination of 3D printing technologies [268], nanoscale 3D printing could see commercial success within the next 10 years, while stereolithography, binder jetting, and material extrusion methods can see

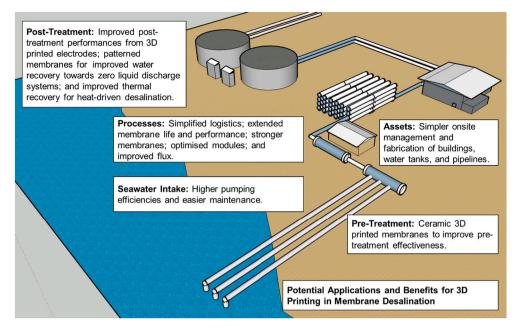


Fig. 20. Overall benefits of 3D printing and its potential future applications and benefits for the entire system.

between 2 and 5 years towards successful commercial 3D printing applications [268]. The most well-established sectors for 3D printing are its services provision and model creation software. The advanced development of 3D printing software can help simplify the design, conversion, and fabrication of much more complex membranes at the nanometre scale without having the need to create large files. Meanwhile, there is yet to develop a software which specifically designs and optimises desalination components that could easily be transferred to the printer for fabrication. Nevertheless, 3D printing research today yields promising potential to simplify manufacturing of complex membrane desalination components and logistics networks around desalination plants.

This review paper explores the potential applications for 3D printing technologies in other parts of the desalination plant from spacers, modules, pretreatment membranes, and infrastructure 3D printing. It is posited that 3D printing application for desalination will promote the digitisation of plants, improve the efficiency of desalination processes, contribute to more sustainable construction and manufacturing processes, and help aid in the reduction of energy consumed for desalination. These solutions offered by 3D printing can make desalination more widely accessible to communities particularly those in developing countries who lack access to basic infrastructure, where small-scale plants could potentially be 3D printed on the spot and also have spare parts fabricated at the exact same location. Although, 3D printing for desalination is still in its infancy, currently, there is growing momentum in the area of 3D printing technologies for desalination. And as the world's water scarcity becomes more severe by the day, 3D printing technologies may be the answer to the world's water shortage problems. These points are visually summarised in Fig. 20.

4. Conclusions

3D printing technologies open up a world of opportunities in the design, customisation, development, testing, and exploration of newer and improved membranes and its associated components for commercial use. This review has addressed some challenges covering aspects of the experiments that have not been successful due to the inherent limitations of current 3D printing materials and technologies, and in current literature dealing with 3D printing technologies for membrane water desalination. The use of 3D printing currently sees higher potential for

spacers and membranes than modules. This is because presently, there is very little desalination studies done on the performance of 3D printed membrane modules. While DLP and CLIP show a more promising outlook in the fabrication of membranes mainly due to the higher resolutions and continuous production capabilities for membrane production scalability. It is estimated that by 2030, the cost of 3D printing will be reduced by between 50 and 75% on a BVUC basis, however, limitations in terms of scalability and resolutions will hinder the adoptability for 3D printing technologies in membrane fabrication. Future perspectives are provided to enhance the success for membrane fabrication using 3D printing.

CRediT authorship contribution statement

Allan Soo: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing - original draft.

 $\bf Syed~Ali:$ Formal analysis, Investigation, Methodology, Validation, Writing - review & editing.

Ho Kyong Shon: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing - review & editing; Supervision, Project administration, Resources, Funding acquisition, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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