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1 **3D Printing for Membrane Desalination: Challenges and Future Prospects**

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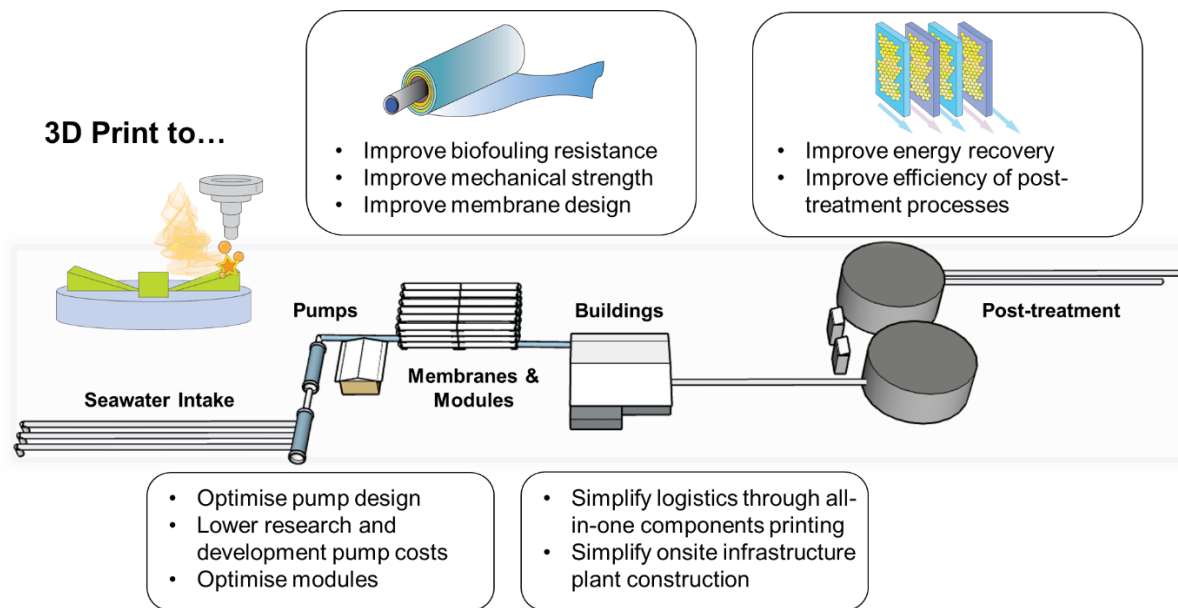
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9 ***Abstract***

10 Recent years have shown a growing interest in the field of 3D printing for applications in the
11 area of water treatment and desalination. The applications for 3D printing are applicable on
12 numerous levels from membranes, spacers, modules, and entire plants; thanks to the high level
13 of customisation, improving resolutions, low-cost to prototype and test designs, sustainability
14 benefits, and reduced time and costs to fabricate new components for desalination. Previous
15 review papers have discussed 3D printing for membrane desalination with a focus on
16 membrane components and additive fabrication methods. This paper addresses the current
17 limitations faced by 3D printing for water desalination and finally provides future perspectives
18 that could address these barriers. The primary goal for this work is to compare and review the
19 current limitations faced by 3D printing technologies in membrane desalination and provide
20 future perspectives in order to improve its adoptability in the industry. The identified barriers
21 include: insufficient resolutions; build volume scale; production rates; appropriate materials;
22 costs; mechanical strength; thermal, mechanical, and chemical stability, which are factors that
23 impede the successful application of 3D printing in membrane water treatment and
24 desalination. Meanwhile, future directions are proposed based on the current trends in
25 membrane research and 3D printing technologies available.

26 **Graphical Abstract**

27



28

29 **Highlights**

- 30 1. Applications for 3D printing across the entire desalination plant process was reviewed.
- 31 2. 3D printing costs are forecasted to decline by approximately 50-75% over the next decade.
- 32 3. 3D printing will expand membrane, spacer, module, and plant designs and optimisations.
- 33 4. 3D Printing will lead to lower operating, research, and engineering and procurement costs.
- 34 5. Spacers lead commercialisation efforts for 3D printing in RO membrane desalination.
- 35 6. 3D printing could potentially expedite the commercial viability of emerging desalination
- 36 technologies.

37 **Keywords:**

38 3D Printing; Membrane Desalination; Modules; Spacers; Membranes.

39

40

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

42

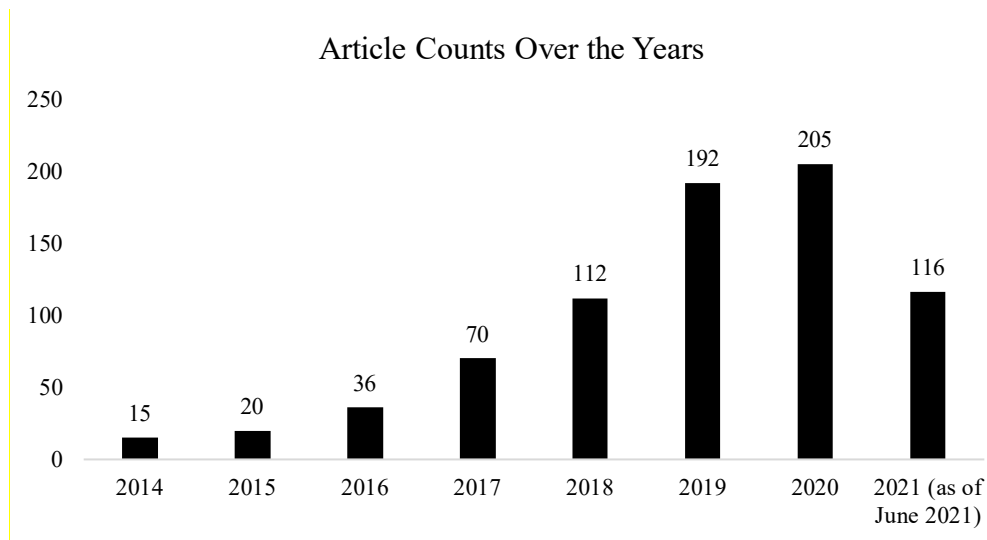
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44 *1.0 Introduction*

45 With a growing demand on the world's water resources and the potential economic impacts on
46 the failure to tackle this problem, governments around the world are finding solutions to
47 safeguard this precious resource. According to the World Bank, climate change has induced
48 water shortages that could cost a country up to 6% of their Gross Domestic Product, heighten
49 the risk for conflicts, force human migration between different regions, increase risks for
50 droughts, and raise food prices [1]. Desalination is one solution to this issue which capitalises
51 on the vast water reserves of the ocean that covers 70% of the world's surface – however, less
52 than 3% of this is drinkable and 2% of it is actually frozen [2]. Cumulative freshwater
53 consumption rose from 46.6 million m³ per day to 67.3 million m³ per day between 2005 to
54 2009 [3], proportionally with the growth in population, infrastructure, and industrialisation. By
55 2017, the daily water consumption rose to 99.8 million m³ per day [4]. This strain on water
56 supply has prompted a need to develop innovative technologies that will improve global water
57 supply, affordability, and accessibility.

58 Research into 3D printing for membrane desalination has garnered growing interest over the
59 past years. Conducting a bibliometric analysis using SCOPUS to identify the trends and with
60 the key search terms TITLE-ABS-KEY("Water" AND "Membrane" OR "3D Printed" AND
61 "3D Printing"), the number of articles published has grown (Fig. (1)). The topic of 3D printing
62 for membrane desalination has grown interest particularly in the area of membrane feed spacer
63 design. Although this area of research is still in its infancy stages, the application of 3D printing
64 technologies towards improving water treatment and desalination technologies remains highly
65 promising due to the limitless applications in the design and optimisation of membrane
66 modules and spacers.

67



68

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

71

72 Since its inception in the mid-1980s, 3D printing has benefited a wide range of industries.
 73 Stereolithography (SLA), fused deposition modelling (FDM), and digital light processing
 74 (DLP) are the three major 3D printing technologies which are forecasted to dominate the
 75 defence, healthcare, pharmaceutical, automotive, and aerospace industries [5]. The technology
 76 - when applied to the membrane desalination industry - could reduce energy demands for
 77 desalination processes by between 15-20% due to more efficient membrane designs [6], lower
 78 manufacturing energy demands by 50% [7], lead to more environmentally friendly and easier
 79 to maintain equipment [8]. The use of ash and slag [9], biodegradable materials [10] [11] [12],
 80 recycled 3D printing material [13], and wood fillings [14] are other environmental advantages
 81 from using 3D printed materials. When applied to manufacturing, 3D printing has the potential
 82 to reduce costs of between US\$ 170 - 595 billion, energy consumption by 2.54 - 9.30 EJ, and
 83 CO₂ emissions by 130.5 – 525.5 MT by 2025 [15]. The adoption of 3D printing technologies
 84 for membrane desalination is still in its early research stages, while the industry still grapples
 85 with its widespread adoption.

86

87 From 2010, the market for 3D printing grew at an average rate of 27.4% to \$12.8 billion in
88 2020 [16]. It is expected that the 3D printing market will grow by 23.2% [17] with a forecasted
89 compound annual growth rate (CAGR) of 14-23.5% between 2021-2027 [5] [18]. Nanosun,
90 one of the earliest pioneers to use 3D printing electrospinning techniques to commercialise its
91 membranes, have so far serviced 15 plants [19]. Unlike conventional 3D printing,
92 electrospinning does not produce finely controlled features and its concept has been around
93 since the late 1800s, with publications only beginning to exponentially grow commencing 1995
94 onwards [20]. Nevertheless, 3D printing is expected to become an essential technology for
95 organisations looking to gain economic and environmental benefits for the foreseeable future.

96

97 Currently, 3D printing applications towards membrane desalination is a new area of study that
98 is gaining traction, with the majority of studies done towards spacers [21] [22] [23] [24] [25]
99 [26] [27]. 3D printed spacers have been found to reduce fouling and scaling, promote flux by
100 creating higher fluid flow unsteadiness and shear stress. Feed spacers with complex geometries
101 were designed to optimize the membrane channel hydrodynamic that would otherwise have
102 been impossible to fabricate using conventional means. The combined use of fluid dynamic
103 models to determine the design features and geometries [28] [29] provides a topological
104 blueprint for further fabrication and enhanced cross-compatibility with other membrane
105 components down the supply chain. To date, there are no studies conducted solely on 3D
106 printed membrane modules across all types of desalination technologies despite the potential
107 with current AM; and no successfully and commercially made 3D printed membrane which
108 utilises conventional 3D printing technologies has ever been achieved. Meanwhile, 3D printing

109 for spacers and infrastructure [9] [30] [31] do exist, although very few literature sources exist
110 for modules and 3D printing desalination membranes due to its technical limitations.

111 Many technologies have been proposed in the fabrication of membranes, however, currently
112 the production of membranes remains out of reach due to the small pore sizes required on the
113 order of less than 1 μm . Tumbleston et al. [32] proposed the use of Continuous Liquid Interface
114 Production (CLIP) for much larger production of parts. This eliminates any potential defects
115 resulting from the presence of air bubbles compared with DLP technologies where the platform
116 is lifted out of the vat resin bath and then resubmerged into the resin solution for another layer
117 to be cured. This production technique was also proposed for the fabrication of membranes by
118 Meham et al. [33]. CLIP allows for the potential to fabricate membranes to infinite lengths
119 and unlike DLP, does not require any stoppages to separate repeating parts from the base
120 platform. Compared between DLP where entire flat sheets can be cured using a UV-LCD
121 screen, a major limitation with using CLIP is the Z-axis vertical layer build time as opposed to
122 the layer curing times inherent within DLP systems which is still low. For modules, where
123 resolution requirements for current 3D printing technologies are not a barrier to its fabrication
124 [34], the technologies exist for a wide range of applications but are not studied due to the
125 established existence of RO modules and the temperature sensitivity of 3D printing polymers
126 for membrane distillation (MD).

127 Previous review articles have examined the applications of 3D printing at a component level,
128 with focuses being on membranes, spacers, and modules. These review papers [34] [35] [36]
129 [37] [38] [39] [40] discuss the applications of 3D printing for membrane desalination from a
130 manufacturing perspective and how these could be applied to the fabrication of membranes,
131 modules, and spacers. Where prototyping and advanced additive manufacturing techniques
132 could expand the prototyping and design capabilities of 3D printed components for membrane
133 desalination plants, no such review paper has yet to discuss the implications of 3D printing on

134 entire desalination plants across pre-treatment, membrane reverse osmosis, and post-treatment
135 stages. Currently, 3D printing research interest is more focused on the development and design
136 of improved desalination performances at the lab-scale by changing spacer and membrane
137 characteristics, with no study to date solely focused on 3D printed modules and its impacts on
138 membrane desalination technologies. This review paper examines and discusses the key
139 barriers 3D printing faces during its applications towards membrane desalination, while
140 providing future directions on what current research activities in this space can deliver to an
141 entire membrane desalination plant. This review paper is unique in that 3D printing
142 technologies have rarely been discussed with its wider applications towards desalination plants
143 throughout its system, despite the rapid growth and importance being put on 3D printing by
144 companies to reach environmental and economic objectives. Another unique dimension to this
145 review paper is that it identifies barriers across membrane, component, and plant assets
146 encountered when adopting 3D printing technologies. This paper also provides future
147 directions to current research using 3D printing applications to overcome these barriers, leading
148 to realisable benefits for operators of the desalination plant from construction to its operational
149 phase.

150

151 ***2.0 Overview of Current 3D Printing Technologies used for Membrane Desalination***

152

153 Over the years there has been a shift towards the use of lasers to cure resins at high precisions
154 and resolutions. Although, FDM continues to remain the cheapest form of 3D printing
155 technology for the fabrication of larger components requiring less stringency on resolution,
156 while laser-based 3D printers are used for the design and fabrication of intricate models. 3D
157 printing technologies can be categorised, and have been applied in the following [41] [42] [43]
158 [44] [45] [46] [47] [48] seen in Table 1, Table 2, Fig. 2 and Fig. 3.

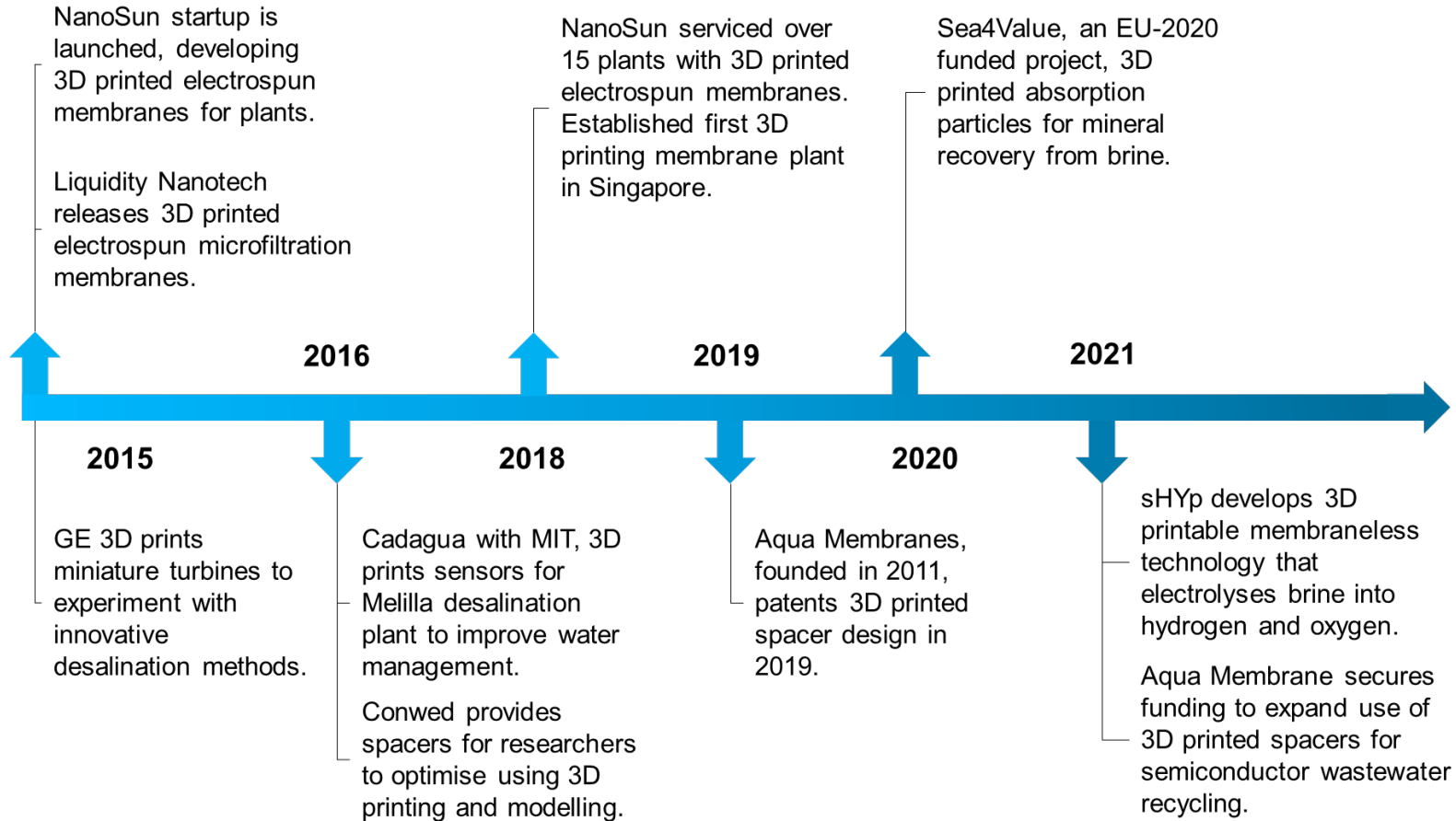
159 Table 1: Overview of 3D printing technologies and its advantages, disadvantages, and applicability within membrane desalination plants.

3D Printing Technology	Additive Description	Print Resolution XY/Z	Advantages	Disadvantages	Desalination Applications				
					Membranes	Spacers	Modules	Minor Infrastructural Assets (i.e., pipes and turbines)	Major Infrastructural Assets (i.e., buildings and water tanks)
3D Construction Printing (3DCP)	<ul style="list-style-type: none"> Concrete is extruded through movable nozzle. Contours/trails are printed stacked to create final model. 	>1,000 μm	<p>Print large structures.</p> <p>Readily use cement mixtures.</p>	<p>Large printers.</p> <p>High cost.</p> <p>Inconsistent structural integrity.</p> <p>Requires correct viscosity for proper print.</p>	×	×	×	×	✓
Digital Light Processing (DLP)	<ul style="list-style-type: none"> UV screen pixels cure photopolymer resin. Cured every layer along Z-axis. 	15-100/5-25 μm	High micrometre resolution.	<p>Low build volumes and scalability.</p> <p>Limited to materials curable by UV light.</p> <p>Toxic resins.</p>	✓	×	×	×	×

Direct Inkjet Writing (DIW)	<ul style="list-style-type: none"> Deposits droplets of material onto surface. Substrates or polymers receive droplets. 	>300/NA dots-per-inch (DPI)	<p>Mature technology (i.e., office printer).</p> <p>High scalability.</p> <p>Low cost.</p>	<p>Only used for surfacing.</p> <p>Bonding strength dependent on surface functional properties.</p>	✓	✗	✗	✗	✗
Fused Deposition Modeling (FDM)	<ul style="list-style-type: none"> Thermoplastic extruded through heated nozzle. Nozzle lays polymer trails for every Z-axis. Layers of stacked trails/contours create final model. 	>200/>100 μm	<p>Low-cost and scalable.</p> <p>Printer simple by construction.</p> <p>Wide range of thermoplastics.</p>	<p>Low resolution.</p> <p>Porosity affects mechanical strength and swelling.</p> <p>Not thermally resistant.</p>	✓	✓	✓	✓	✗
Metal Powder Bed Fusion (MPBF)/Selective Laser Sintering (SLS)	<ul style="list-style-type: none"> Layers of fine powders are sintered together. High-powered lasers used to sinter. Roller replenishes process. 	300/100 μm	<p>Complex metallic geometries.</p> <p>Use of metallic alloys with corrosion resistance.</p> <p>Little to no support required.</p>	<p>Longer print times.</p> <p>May require surface treatment for corrosion resistance.</p> <p>May require further surface finishing.</p>	✓	✓	✓	✓	✗

			<p>Powder can be reused.</p>	<p>Lower mechanical strength than subtractive processes.</p> <p>Energy intensive.</p> <p>Part distortion.</p>					
<p>Multijet Modelling (MJM)/ Multijet Printing (MJP)/ Polyjet</p>	<ul style="list-style-type: none"> Wax droplets deposited and cured with UV light every layer. 	<p>600 – 1200 DPI/>16 μm</p>	<p>Hardness adjusted through feed mixture ratios.</p> <p>Suitable for creating composite models.</p> <p>Good surface finish.</p> <p>Wide range of colours.</p> <p>Good chemical resistance.</p> <p>High mechanical consistency across model.</p>	<p>Support material can cause undesirable properties.</p> <p>Cannot produce sharp corners.</p> <p>Strength dependent on additive polymeric binder.</p> <p>High capital cost.</p>	✓	✓	✓	✗	✗
<p>Stereolithography (SLA)/ vat-</p>	<ul style="list-style-type: none"> Laser spot cures resin for each layer Platform moves down 	<p>25-50/25-300 μm</p>	<p>High micrometre resolution.</p> <p>Good surface finish.</p>	<p>Toxic resins.</p> <p>Low mechanical strength.</p>	✓	✓	✓	✗	✗

photopolymerisation/micro-stereolithography (MSLA)	Z-axis after each curing.			Low thermal resistance. High capital cost for larger printers.					
Two-Photon Polymerisation (2PP)	<ul style="list-style-type: none"> Resin is cured at the electron-scale. Sum of two-photons being absorbed within lead to curing. 	<1/<1 μm ~0.2-0.3/~0.2-0.3 (specified)	High nanometre resolution.	Cannot produce large models. High capital cost.	✓	✗	✗	✗	✗



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

164 Table 2: Recent membrane desalination research papers dealing with 3D printing technologies and the challenges, advantages, and disadvantages
 165 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]

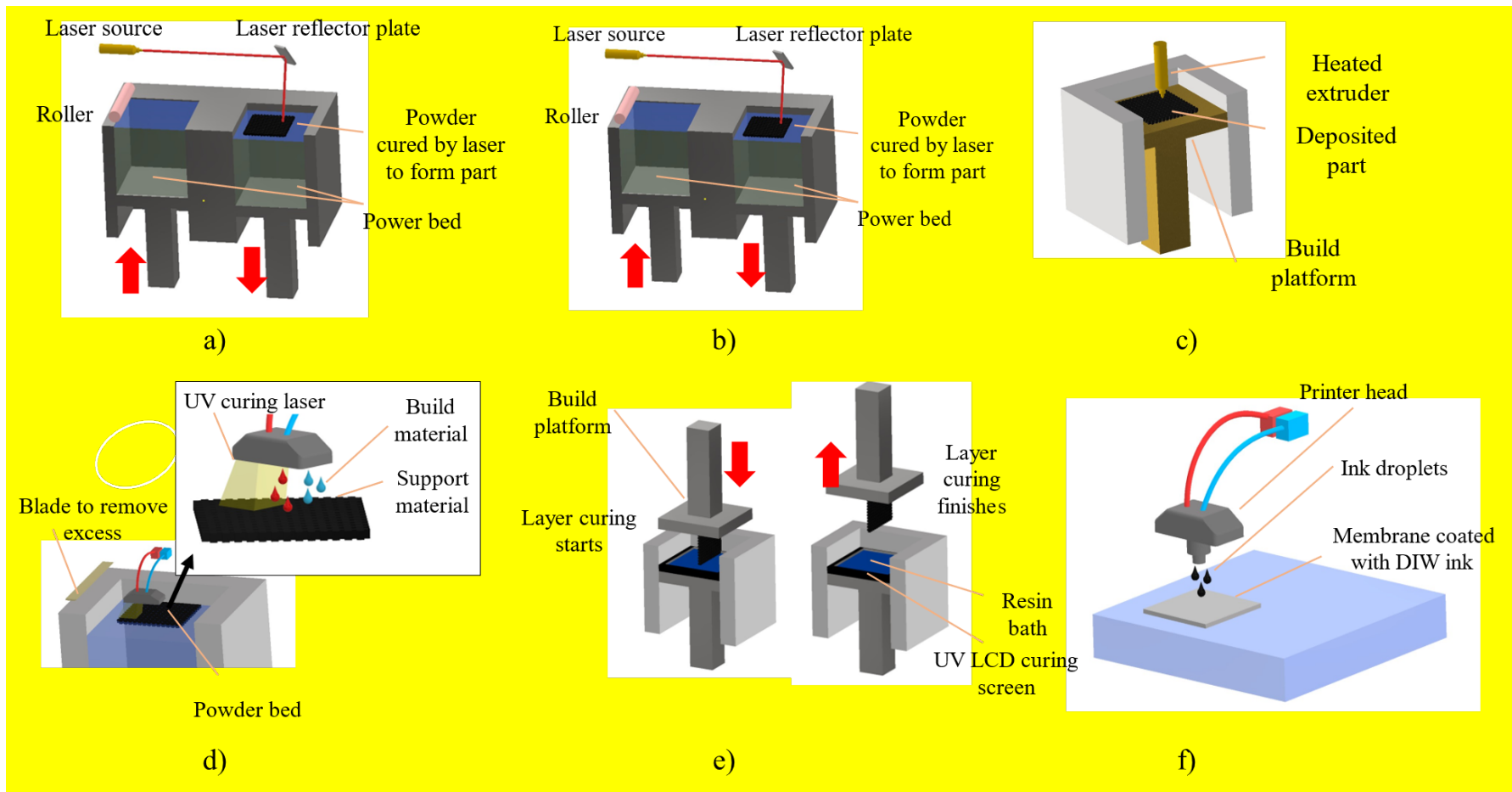
Filtration (spacers)	DLP	Complex spacers and features printed.	Improved flux. Lower energy consumption/ Reduced fouling.	Potential localised fouling.	[50]
Filtration (spacers)	MJM	Microfabrication of spacers.	Improved flux. Micro-features produced.	Increased pressure drop.	[51]
FO (spacers)	MJM	Complex, 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]

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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).

171 ***2.1 Barriers and Benefits Towards Additive Manufacturing for Membrane Desalination***

172

173 There are of course, several challenges facing the use of 3D printing for direct membrane
174 fabrication. Although, electrospinning could be considered a form of 3D printing technology,
175 the lack of direct controllability of the membrane's morphological features is a primary
176 limitation where generally, only the thickness up to a certain point can be controlled. It is the
177 poor resolution, limited selection of materials, slow printing, high recurring and upfront costs,
178 safety and environmental concerns, and industrial scalability barriers: that all pose challenges
179 to its wider adoption in the membrane fabrication industry [35]. 3D printing using ceramics
180 have several limitations including direct printing control of the membrane morphological and
181 topographical features compared with thermoplastic- and photopolymer-based printers. Like
182 polymer-based 3D printers, the high costs, low resolutions, and the infancy stages for this
183 technology are what prevent it from advancing to a more mature technology status. For all 3D
184 printers, the advantages allow for the fabrication of membranes outside the traditional designs
185 of flat sheet, tubular, and hollow fibre configurations, and the possibilities to design, optimise,
186 redesign, retest, and deploy at much cheaper costs compared to subtractive or chemical
187 reactions. 3D printing with embedded ceramic materials have been done in the past using
188 alumina and silica nanoparticles in membranes [60] [61] [62] [63], although the use of ceramic
189 as a general material in all aspects of desalination is costly compared to its polymeric
190 counterparts.

191

192 The barriers to 3D printing vary depending on the type of application. For thermal-based
193 desalination, temperature resistance will be a highly desired property for the printed
194 component. Meanwhile, in pressure-driven desalination, mechanically strong and stable
195 components will take high priority. For membranes, superhydrophobicity will find better

196 applications for MD compared to RO, where hydrophilic materials are needed. However,
197 throughout all membrane desalination applications, the universal barriers to the application of
198 3D printing are resolution, cost, industrial scalability, and chemical stability. Much larger
199 components will find less importance in resolution such as modules and water tanks, while
200 resolutions in fabricating membrane pores and microfeatures that produce reliable sources of
201 safe, drinkable water will be extremely important.

202

203 *2.1.1 Cost*

204

205 The design and production of complex 3D printed membrane desalination components paves
206 way for economically beneficial opportunities for the desalination industry's plant operators
207 and membrane manufacturers. A recent study cites that the cost of SLS and FDM 3D printed
208 parts could be reduced by 10% and 70-80% respectively when polymeric feed materials are
209 reused in the circular economy [64]. Taking advantage of the increasingly sustainable reuse of
210 3D printer polymeric materials, membranes can then be reformed into complex shapes that
211 prolong the operating life of membranes and minimise cleaning frequencies and costs.
212 However, the use of virgin plastics for 3D printing is still some of the most expensive, costing
213 around \$US250/kg for FDM printers [38], while the printers can cost a lot more on the order
214 of several thousand dollars with limited build volume space. Meanwhile, productivity
215 improvements through the use of 3D printed spacers can be as high as 93% [51], indicating
216 that the main benefits will arise from the long-term savings that 3D printed spacers can have
217 on desalination systems such as the specific energy consumption, flux, and minimal cleaning
218 maintenance.

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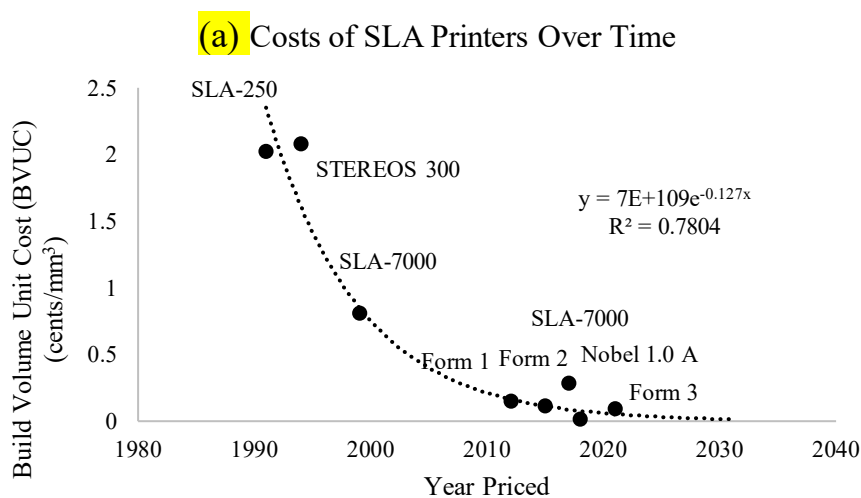
220 The direct fabrication of membranes using 3D printing is still a farfetched reality. When
221 compared with phase inversion and electrospinning, 3D printing loses out in terms of material
222 consumption costs, build time, and resolution. Depending on the type of desalination, flawless
223 nanometre resolutions are required with the general trend that the higher the resolution for a
224 3D printer, the more expensive it becomes. Presently, the Photonic Professional GT2 can cost
225 half a million euros to procure with very little productivity gains, with the suppliers citing that
226 to fabricate a membrane it will take 24 days per mm³ volume of printing as quoted by
227 Nanoscribe. This is given that the resolution of the printer is rated at 400 nm and costs around
228 \$500,000 [65]. This becomes an uneconomically feasible feat for membrane fabrication, and
229 there is a long way ahead towards 3D printers capable of printing repeatable parts at nanometre
230 resolutions that are necessary for RO applications. DLP printing, on the other hand, is a more
231 promising alternative which cures photopolymeric resin on a layer-by-layer basis. However,
232 the smallest resolutions for DLP printers are on the order of 15-25 microns that are presently
233 available on the market (Kudo3D Micro SLA and MakeX PRO25 DLP printers), which
234 currently cost between \$8,700 - \$US10,000 [66] [67], and have maximum build volumes of
235 around 48 mm × 27 mm for both – too small for any acceptable commercial application.
236 Presently, FDM printers are some of the cheapest 3D printing technologies that can be
237 purchased from the market and experimented with previous studies [68] [43] [69] which
238 expand opportunities towards using macroscale experiments for membrane desalination. FDM
239 parts were found to contain the lowest resolution, however, FDM is regarded as the most
240 affordable form of 3D printing technology on the market with prices falling from \$US50,000
241 from nearly 30 years ago to around \$US300 today [69].

242

243 It is forecasted that the cost of 3D printers will decline in the coming years just as it has been
244 for the past three decades. The declining costs in 3D printing, combined with its improving

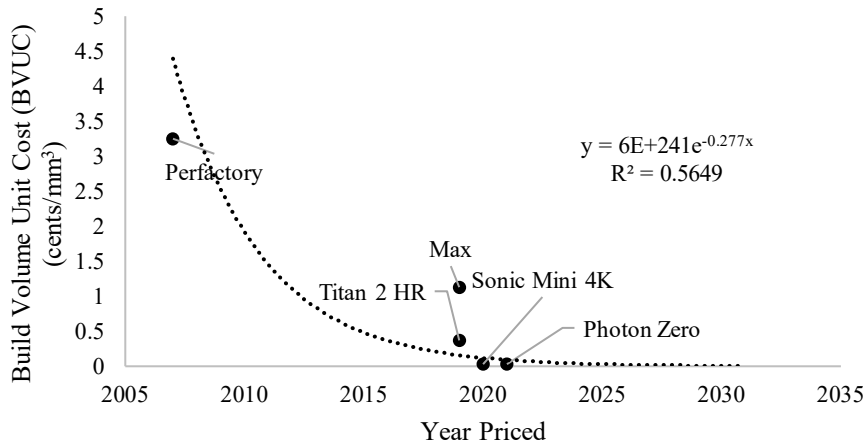
245 resolutions, make it an attractive technology for the production of affordable, high-resolution
 246 membranes requiring complexity at the microscale. During the emerging period of 3D printing,
 247 the cost of printers can range from \$10,000 all the way up to \$500,000 [70]. Over the next
 248 decade, it is estimated that the cost of 3D printing will be reduced by between 50-75% (Fig.
 249 (4)). In these cases, the costs should not increase while increasing the build volume of the
 250 printers and its resolutions. The decline in build volume unit costs (BVUC) was more
 251 pronounced in DLP printers falling from 3.25 cents/mm³ with the EnvisionTEC Perfactory to
 252 0.03 cents/mm³ between 2007 and 2021 – a factor of ~110 reduction. Compared to SLA, a
 253 technology older than FDM, the BVUC has fallen from around ~2 cents/mm³ to 0.002
 254 cents/mm³ in the space from 1991 to 2018 - a 1000 decline in magnitude. FDM started off with
 255 lower BVUC and gradually declined to half the costs compared to that of SLA, from 1.51 to
 256 0.001 cents/mm³ – a reduction by a factor of ~1500 for this period. It is expected that these
 257 declining exponential cost trends will continue into the future with the affordability of 3D
 258 printers becoming a reality for manufacturers, however, scalability in terms of size and
 259 production quantities becomes a real limitation facing 3D printing applications towards
 260 membrane fabrication.

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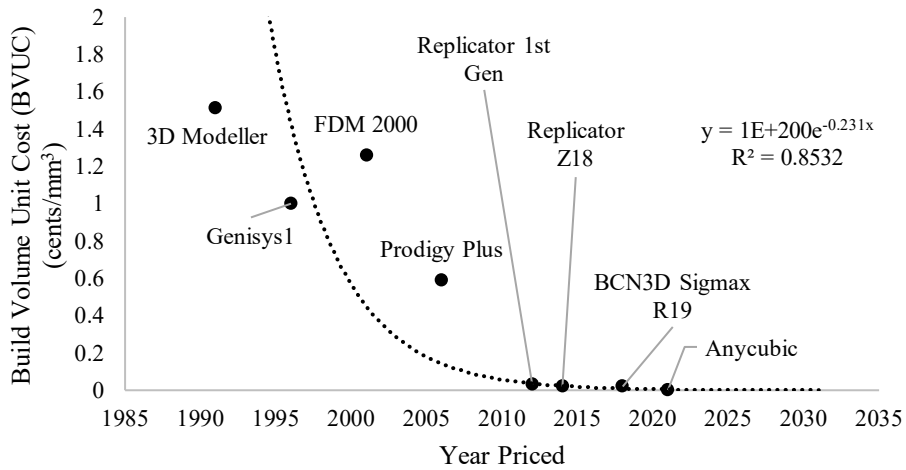
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(b) Costs of DLP Printers Over Time



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(c) Costs of FDM Printers Over Time



264

265 Fig. 4. Prices for 3D printers have dropped exponentially over the past ~35 years, with this

266 trend expecting to continue leading to a reduction in printing costs by 50-75% by 2035 ((a)

267 Costs of SLA Printers Over Time, (b) Costs of DLP Printers Over Time, (c) Costs of FDM Printers

268 Over Time)

269

270 2.1.2 Thermal Stability

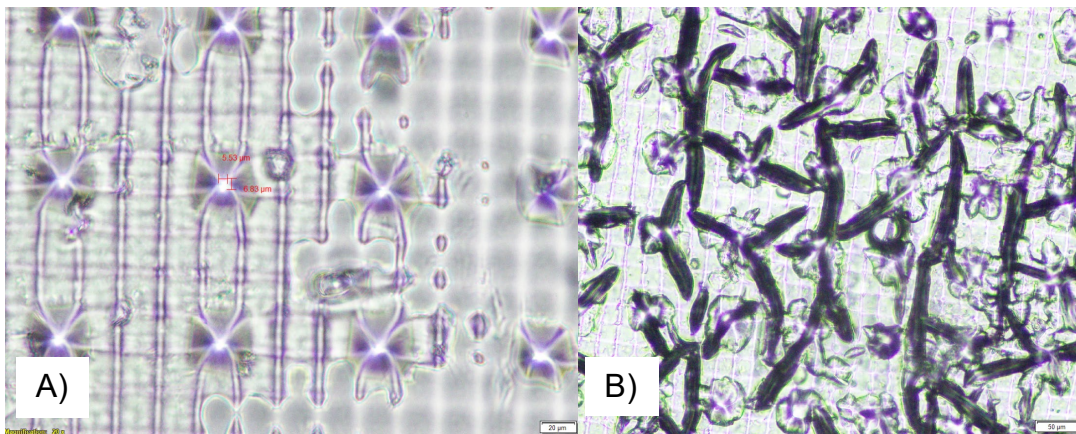
271

272 Polymers offer the most affordable option compared with ceramic materials due to the lack of

273 a need for post-processing (such as sintering). However, there are disadvantages to its use at

274 the micro-fabrication scale in thermally driven desalination environments. Fig. (5) shows the
275 before and after effects of rapidly exposing a DLP 3D printed membrane to a hot feed solution
276 at 50°C. On the contrary, when the feed solution was slowly heated, such micro fractures were
277 averted. This presents a limitation for the application of 3D printing membranes in thermally
278 driven membrane desalination systems, where for every operation, the feed solution must be
279 slowly heated to prevent thermal fractures from happening within the micro-structures and
280 features of the 3D printed membrane. The use of thermoplastics in 3D printing membrane
281 fabrication makes it vulnerable to thermally driven processes, leading to significant membrane
282 warpage and catastrophic failure over longer periods of operation.

283
284



285

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

289

290 2.1.3 Mechanical Strength

291

292 Mechanical strengths among polymeric printers are substantially weaker compared with SLS
293 using metallic powder as the membrane material. The material's bulk modulus for expansivity,

294 the durability of the material when submerged in water for long periods of time, and whether
295 hydrolysis can occur are key considerations in the use of membranes for desalination. Due to
296 the sintering behaviour of powders, the resolutions of 3D printers would be lower compared
297 with thermoplastic- and photopolymer-based 3D printing technologies. This is because the SLS
298 resolution depends on the size of the powder particles and the laser spot size, with typical SLS
299 resolutions being around 70-100 μm and powder particle sizes of 5-20 μm [71] [72] [73]. This
300 makes it highly compatible with the design and fabrication of spacers and modules that are
301 mechanically sturdy but do not require extremely detailed features.

302

303 Wittbrodt and Pearce [74] studied the effects of colour and strength on 3D printed parts. The
304 variations in crystallinity within the part were a cause for concern where non-uniform 3D
305 printed structures were more susceptible to mechanical failures. The orientation of internal
306 structures for a printed part were evaluated by Letcher and Waytashek [75], the printed tensile
307 strength for a 45° raster component was 64 MPa, compared to 0° and 90° raster orientation and
308 a tensile strength of 58 and 54 MPa respectively. Mechanical strengths were also determined
309 by the thickness of the printed layers [76] [77], where smaller thicknesses led to higher
310 mechanical strengths. The study [74] highlights the importance that the addition of chemicals
311 plays in altering the internal crystalline structure for a 3D printed part. In membrane
312 desalination, it is highly unlikely that colour will be important, however, chemicals that
313 improve the hydrophobicity or hydrophilicity of a component must not be used to the detriment
314 of mechanical strength. These include the formation of voids which can lead to long-term
315 degradation in mechanical integrity [13] [78]. Designers of membrane components can
316 experiment with different layering and structural designs using their printers, while smaller
317 layer thicknesses may help alleviate some of the weaknesses arising from the development of
318 resins that print mechanically weak, amorphous structures. Consequently, smaller layer

319 thicknesses and higher fill volumes lead to longer print times, leading to lower productivity
320 and commercial viability. Mechanical sturdiness is determined by layer thicknesses, print
321 times, chemical additives used, porosity, and the design of internal structures for the printed
322 part. Mechanical strength will strongly influence the selection process for viable resins and
323 printing technologies.

324

325 Post-processing steps can be taken to improve the mechanical strength of a 3D printed part. In
326 DLP and SLA printing, parts can be cured under UV light for a period of time. Longer curing
327 times improve the mechanical strength for the part and was demonstrated in Kim et al. [79]
328 when curing times were raised from 60 to 90 mins, leading to an improved flexural strength
329 from 120.93 MPa to 131.94 MPa. Raising the curing time will lead to greater brittleness of the
330 printed model, which is undesirable for fabricating modules which require high flexural
331 strength [80]. Changing the printing conditions such as raising the resin bath temperature and
332 reducing its viscosity can lead to stronger prints [81]. The disadvantage to using this approach
333 is reduced resolution due to the resin's lack of affinity for separation from the printed part after
334 each curing stage, leading to unwanted cured features. Resolutions for membrane modules
335 need only to be sufficient enough to prevent the leakage of water during pressurisation. While
336 smaller detailed features such as membranes will face significant challenges in producing
337 highly detailed nanoscale features combined with high mechanical strength comparable to
338 composite, asymmetric, and symmetric RO membranes. Another barrier is the rigidity of the
339 models that can be fabricated. In some cases, flexibly rolled membranes for example, are
340 desired in RO when fitted to standard cylindrical modules, while plate-and-frame designs are
341 more feasible for flat membranes. Given that the RO industry has followed the same module
342 design conventions, the fabrication of membranes with consistently high flexural strength for
343 example, poses another barrier. Table 3 shows the range of printing materials available,

344 including the metallic alloy Inconel and 2PP materials exhibiting the greatest thermal resistance
345 properties in the table. A combination of uniquely developed 3D printing materials that is
346 crystalline combined with strong cross-sectional design for printed components are some
347 solutions to overcoming barriers relating to low mechanical strength. The pressures required
348 to be withstood for RO membranes, modules, vessels, piping, and auxiliary equipment is 98
349 bars/9.8 MPa [82], and Table 3 shows the tensile strengths of the 3D printable materials
350 currently available that are exceedingly well above the operating pressures of 70 bars/7 MPa
351 suitable for modules. However, it remains uncertain whether creep deformation of 3D printed
352 plastics could happen during prolonged RO operations.

353

354

355

356 Table 3: Mechanical tensile properties of the 3D printing polymeric materials compared with commonly used materials within the desalination
 357 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 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 minutes 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 resistance. Cryogenic environments applicable.	
IP-G	-	3.4	AM, 2PP	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 fibre 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 watertightness, 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 properties, and good dimensional accuracy.	[100]
Polyethersulfone	85	2.4	Conventional	High resistance to heat, impacts, acids and bases. Is hydrolytically stable against hot water and steam. Good electrical properties.	[101]
Poly-lactic acid (PLA)	50.84-57.16	-	AM, FDM	Bioplastic and biodegradable, low thermal resistance and malleable under high heat, low mechanical strength, can be reused.	[74]
Polypropylene	21.4	0.907	AM, SLS	Tough, fatigue-resistant, functional applications, for components,	[93]

Polypropylene (atactic)	21.4	0.689-1.52	Conventional and AM, FDM	Hydrophilic, high melting temperature, chemically resistant, and good mechanical strength. Used in MF to NF membranes.	[88]
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 tensile strength, stiff, good thermal and chemical resistance,	[93]

358

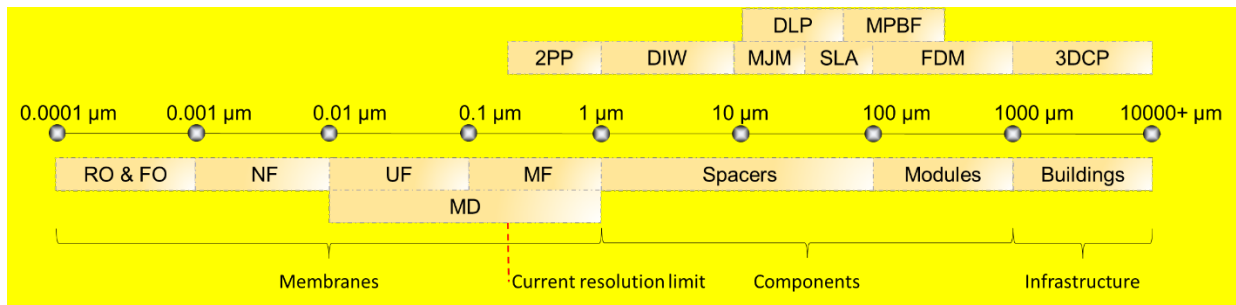
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360 **2.1.4 Resolution**

361

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

385



386

387

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

391

392 2.1.5 Hydrophobicity and Hydrophilicity of 3D Printing Membranes

393

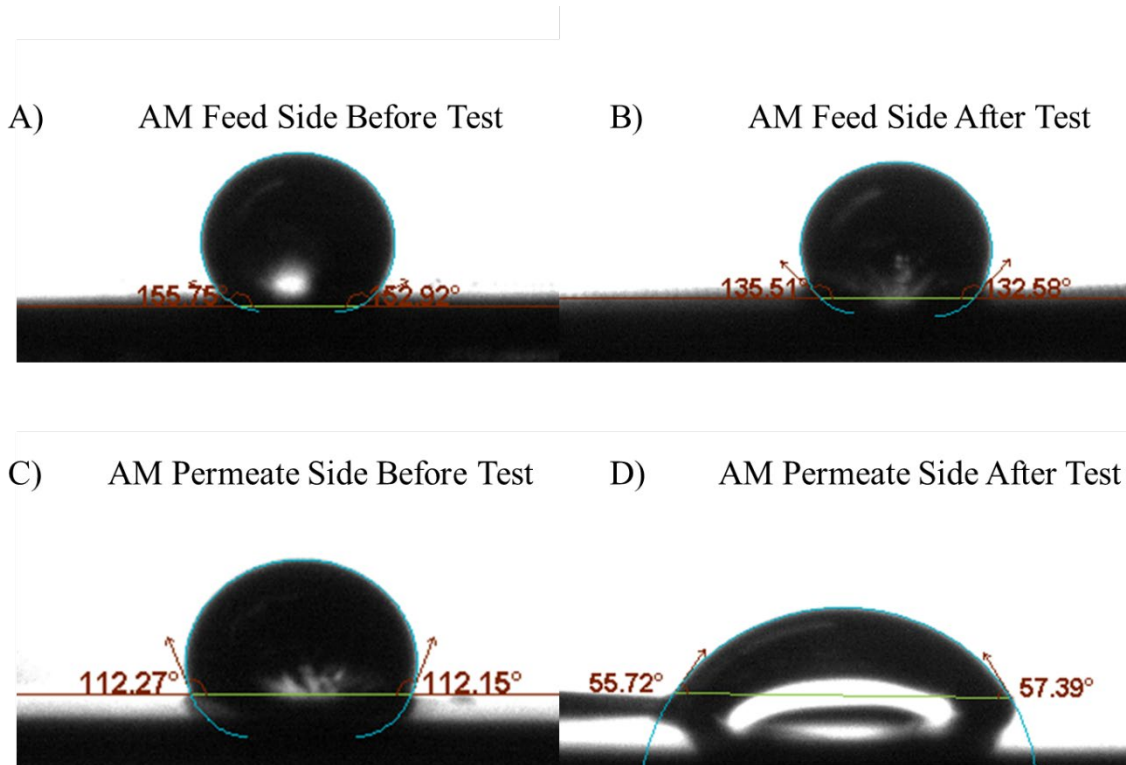
394 Nearly all 3D printed photopolymer resins exhibit hydrophobic properties [109]. Recent 3D
395 printing technologies have allowed designers to impart and design in hydrophobicity and
396 superhydrophobicity onto printed objects. Despite this, 3D printed resins typically produce
397 parts with high surface energy, requiring a second layer of coating that reduces this surface
398 energy to make it more hydrophilic depending on the application. For MD, hydrophobicity is
399 desired over hydrophilicity. While for FO and RO hydrophilicity is preferred. This allows a
400 versatile fabrication of membranes that can achieve both hydrophobic and hydrophilic
401 properties, however, the low surface energy coating can also cover the nano features of the 3D
402 printed membrane and potentially render it less effective [110]. Unlike MD where the
403 membrane interface with the solutions is the important separating factor in allowing only water
404 vapour through, liquid-phase water passes through FO and RO membranes, requiring the entire
405 structure of the membrane to be hydrophilic rather than just the surface coating. Seen in Fig.
406 (7), a partial explanation for this phenomenon is the presence of the smoother side of the

407 membrane when peeled off the supporting plate of the DLP printer. While the rougher side (the
408 side that is last exposed to the LCD UV light) has sub-micron pixel-cured rough features that
409 make it more hydrophobic than the base side. Jafari's et al. [110] study provides suggestions
410 on designing circular protrusions into the membrane which reduces surface hydrophilicity. By
411 printing complex surface features at the sub-micron level, the hydrophobicity of the part will
412 be enhanced even if the material is inherently hydrophilic – greatly expanding the selection of
413 materials to be used for MD. While for RO and FO applications, the hydrophobic nature of
414 photopolymer resins makes it difficult to produce high-performing membranes unless the
415 material is inherently hydrophilic. Therefore, hydrophobic polymers should be used for MD
416 while for RO and FO hydrophilic polymers should be applied, which is the most significant
417 challenge to current 3D printing processes to date for FO and RO. It is anticipated that the
418 resolution, areas of the materials, and the build speed will improve [34] [37].

419

420 Recent advances in 3D printing have expanded its applications towards producing both
421 hydrophilic and hydrophobic resins. In one study, the addition of acrylic acid to the resin
422 mixture poly(ethylene glycol) diacrylate turned the photopolymer superhydrophilic by
423 lowering the wetting contact angle down to 0°, and superhydrophobic using 1H, 1H, 2H, 2H-
424 perfluorodecyl acrylate [111]. These hydrophilic and hydrophobic additives allow tailored
425 solutions to be made that expands applications towards all areas of membrane desalination.
426 Additionally, both superhydrophobic and superhydrophilic materials can be printed on top of
427 one another using P μ SL 3D printing [111]. With high resolutions and multi-material
428 opportunities, it is possible to directly fabricate membranes and desalination components with
429 hybrid superhydrophobic-superhydrophilic properties, although this area of research has yet to
430 be explored. A major possible barrier could lie in the long-term bonding strength between 3D
431 printed superhydrophobic and superhydrophilic materials when fabricating membranes and

432 other components with completely dissimilar surface energies, therefore, covalent bonding
433 between dissimilar surface functional groups could become a barrier to its high performance.
434



435
436 Fig. 7. The hydrophobicity of the MakeX PRO25 and PRO30 printer exhibited
437 superhydrophobic properties on one side of the membrane (a) and hydrophobicity on the other
438 (c), while after the test the membrane on the permeate side lost hydrophobicity (b) and more
439 considerably for d).

440
441 **2.1.6 Chemical Stability**

442
443 The first instance of 3D printed membranes with some degree of chlorine resistance was done
444 by Chowdhury et al. [112], where the electrospaying technique was applied to deposit droplets
445 of trimesoyl chloride (TMC) and m-phenylene diamine (MDP) to react and form polyamide
446 onto the surface of a charged role. The chlorine resistance of polyamide is on the order of

447 between 200-1,000 ppm [113]. While there is no clear definition of chlorine-resistance for
448 membrane desalination [114], membranes can still suffer from gradual degradation and
449 perform either better or worse as a result. Imparting chemical stability can be achieved through
450 surface coatings [115] and chemical modifications [116] [117] [118]. Possibilities for enhanced
451 chemical resistance and stability of membrane can come in the form of chemical surface
452 modifications and the selection of appropriate materials [58] [119]. Ceramic 3D printing is one
453 example of selecting a material that is inherently chemically resistant, where Ray et al. [58] 3D
454 printed ceramic membranes, however, these were brittle and would not be ideal for rolled
455 designs and are more expensive than using polymers.

456

457 It was hinted that certain plastics create leachates that are environmentally detrimental to
458 marine life [120] [121]. Therefore, the chemical stability of a 3D printed membrane and its
459 components cannot come at the cost of polymer leaching into the drinking water supply or
460 environment through hydrolysis or unwanted reactions. FDM using ABS plastics at higher
461 melting temperatures emit higher toxic particulates than PLA that affect respiratory function
462 largely from the printing process [122]. Certain bio-printable plastics, considered safe by the
463 industry, induced developmental toxicity within cell growth and embryos, requiring mitigation
464 through post-processing steps to nullify the dangers [123]. On the other hand, PLA plastic is
465 safe to humans due to its widespread use in food packaging [124], and may be the most
466 appropriate material of choice for developing biodegradable, chemically stable components for
467 desalination plants. Chemically stable components require strong chlorine resistance and non-
468 existent leaching of toxic chemicals into drinking water supplies.

469

470

471 As fouling continues to be an issue for membrane desalination, 3D printing membranes and
472 spacers must be chemically resistant to chemical cleaning agents such as chlorine. Leakage of
473 toxic materials into the drinking water supply is another cause for concern and fortunately
474 enough, many of the polymers in use by the 3D printing industry can be safely consumed given
475 its widespread use in the medical and dentistry industry. Because 3D printing companies are
476 constantly developing unique resin mixtures suited to its own printer models, the chemical
477 resistance and toxicity of 3D printing components and membranes specific to desalination still
478 requires further areas of research.

479

480 **2.1.7 Mechanical Stability**

481

482 Submerging 3D printed polymers in aquatic saline environments can lead to deformities and
483 deterioration in the structural integrity of the printed components. Ayrilmis et al. [76]
484 investigated the properties of FDM printed PLA/Wood composite materials to thickness layers
485 of 0.05 mm to 0.3 mm. PLA/wood composites were submerged for 28 days at 20°C to detect
486 for any swelling. Swelling was more severe with larger printing thicknesses due to water
487 seepage into the pores of the material. Larger thicknesses led to higher porosities, leading to
488 higher water absorption. Within desalination applications, this could create ripe conditions for
489 bacteria and algae to grow within these pores, particularly for spacer fabrication that can
490 contribute to greater biofouling. More undesirably, when fabricating modules that need to be
491 watertight, deterioration in the structural integrity of the module may happen with time leading
492 to fluid leakage. Mechanical stability of 3D printed parts however, can be achieved through
493 post-processing methods such as the application of acrylic-based varnishes that reduce
494 porosities [78]. Mechanical stability issues are less likely to transpire in 3D printing
495 technologies utilising lower layer thicknesses and porosities seen in SLA, 2PP, and DLP

496 technologies where layer thicknesses of less than 50 μm can be achieved. Consequently, the
497 disadvantage of reducing layer thicknesses and porosities is higher material-consumption and
498 longer print times, which conversely and advantageously leads to much more sturdier models.

499

500 *2.1.8 Industrial Scalability*

501

502 With the design and optimisation of new and innovative membrane spacers and modules, the
503 next issue becomes apparent when the mass production of components for the water
504 desalination industry is demanded. Currently, even with the commercial availability of 3D
505 printers and its trend in the drop in prices since the late 1980s and early 1990s, the productivity
506 and speed to which membranes could be fabricated using 3D printers is still low due to the
507 additive layer-by-layer process. The cheapest and lowest resolution 3D printer in this current
508 day operates off DLP technology, has a resolution of 35 microns, a print speed of 80 mm/hr, a
509 build volume of $132 \times 74 \times 130$ mm and has a cost of \$US409 [125]. With large membrane
510 areas on the order of 20 m^2 per module in some cases, the scalability for 3D printing technology
511 is farfetched compared with other methods such as phase inversion and interfacial
512 polymerisation. It is more economical to 3D print larger, lower resolution components for
513 desalination such as modules and spacers than it is for membranes. 3D printing is currently
514 limited to producing small quantities of complex components. Another major issue with 3D
515 printing is repeatability at the nanoscale. Even with pixel- and spot-based printing processes,
516 3D printing repeating nanofeatures at commercial scale is a challenge and even more so when
517 examining for defects due to the myriad of factors that can affect the dimensional accuracy of
518 the nanofabricated part stemming from vibrations and curing irregularities during printing. The
519 challenge here is the development of 3D printers that can fabricate large but highly detailed
520 components at the micrometre and nanometre scale in large quantities. The recent release of

521 the Uniontech RSPRO 2100 SLA printer in 2020, the world's largest 3D SLA printer to date,
522 has a build volume $2100 \times 700 \times 800$ mm and a laser spot size of between 100-850 μm [126].
523 Using this setup, 2.1 m by 0.7 m spacers and multiple modules could be made. Compared with
524 the Stratasys SLA-500 printer released in the 1990s, the build volume is $508 \text{ mm} \times 508 \text{ mm} \times$
525 610 mm [127]. An approximate increase in 1 m^3 was achieved over the three decades for SLA.
526 Meanwhile, much larger 3D printing technologies can have build volumes as big as 10 m^3
527 which can print car-sized models [128]. FDM printers will less likely encounter scalability
528 issues compared with other finer resolution, laser-based printers, where FDM build volumes
529 are determined by the space allowed for a moving extruder, while DLP printers depend on resin
530 bath dimensions, build platform area, and the size of UV LCD screens. Scaling up 3D printing
531 continues to be a major challenge, and this is likely to be more arduous for UV- and laser-based
532 printers compared with thermal extrusion technology.

533

534 *3.0 Future Perspectives for 3D Printing Applications for Water Desalination*

535

536 Tijjng et al. [35] suggested future investigations into the use of combining 3D printing with
537 other traditional membrane and manufacturing processes, and the forthcoming advent of 4D
538 printing where 3D printed features change properties and performances in its operating
539 environments over time (examples including twisting, curling, bending, and folding designs).
540 The combination of traditional membrane fabrication methods such as electrospinning with 3D
541 printers, hybrid manufacturing with subtractive and formative manufacturing approaches, and
542 4D printing – where 3D printed objects can adapt and change with time in the environment,
543 with an example being rotating spiral spacers [54], were proposed. However, these perspectives
544 do not address the material and resolution limitations for the 3D printing fabrication of
545 membranes.

546 Previous 3D printing applications for membrane desalination included the use of TPMS spacers
547 with improved scaling-resistant properties as salinity concentrations increase with time [29]
548 [24] [28] [49] reflecting the advantages of 4D printing, and feed spacers with turbulence-
549 promoting parts [50]. 3D printing for membrane desalination opens up avenues to explore new
550 designs and behaviours when submerged in aquatic environments.

551

552 ***3.1 Membranes***

553 ***3.1.1 Modified Feed Spacers for Anti-Fouling and Flux Enhancement***

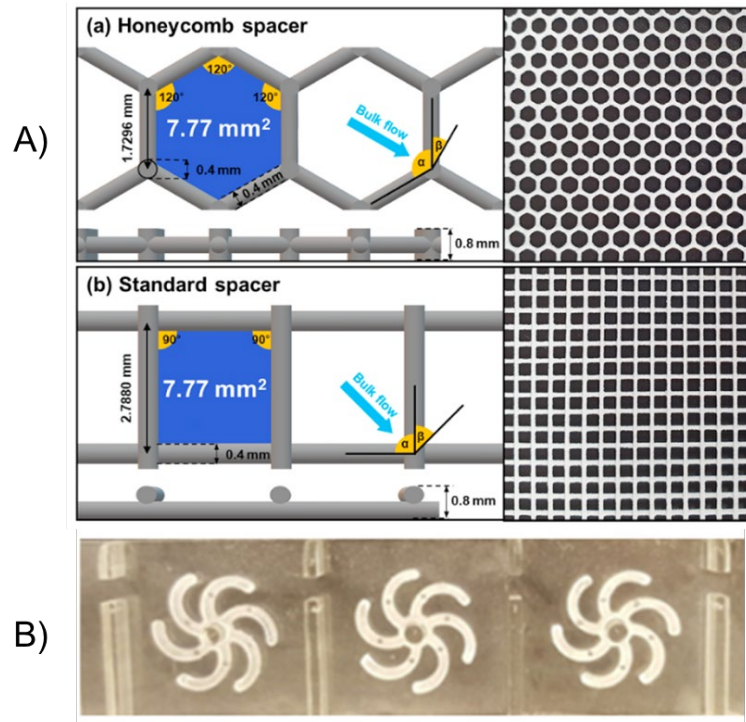
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555 Currently, commercialised direct fabrication of membranes for water desalination is not yet
556 achievable, while for lower resolutions larger components of membrane desalination systems
557 such as spacers can be designed and fabricated using 3D printing technologies such as SLS,
558 DLP, and SLA [21] [24] [56] for enhanced filtration. There are inherent limitations in the use
559 of conventional spacers due to the lack of turbulence-promoting characteristics that help
560 mitigate the onset of fouling and scaling on membranes.

561

562 The incorporation of new and innovative spacers for fouling mitigation has been very
563 promising and can be seen in the studies shown in Table 2 and Fig. 8. The increase in turbulence
564 prevents the adhesion of foulants to the surface of membranes while promoting flux in the
565 process. Therefore, the focus on improving flux and fouling mitigation is shifted away from
566 surface coatings on membranes to turbulence-induction using spacers. In addition, promoting
567 turbulence using spacers has additional advantages towards reducing the concentration
568 polarisation on the surface of membranes [24] and reducing reverse solute flux in FO [53].
569 Conventional feed spacers have limitations when creating flow unsteadiness in the membrane
570 channel, resulting in increased fouling and lower flux. It has been presented in many studies

571 that modifying the geometries of the feed spacers can increase turbulence, however, complex
572 geometries are difficult to produce using conventional techniques. 3D printing technology can
573 therefore be used to fabricate complex spacers to enhance filtration and desalination
574 performance.

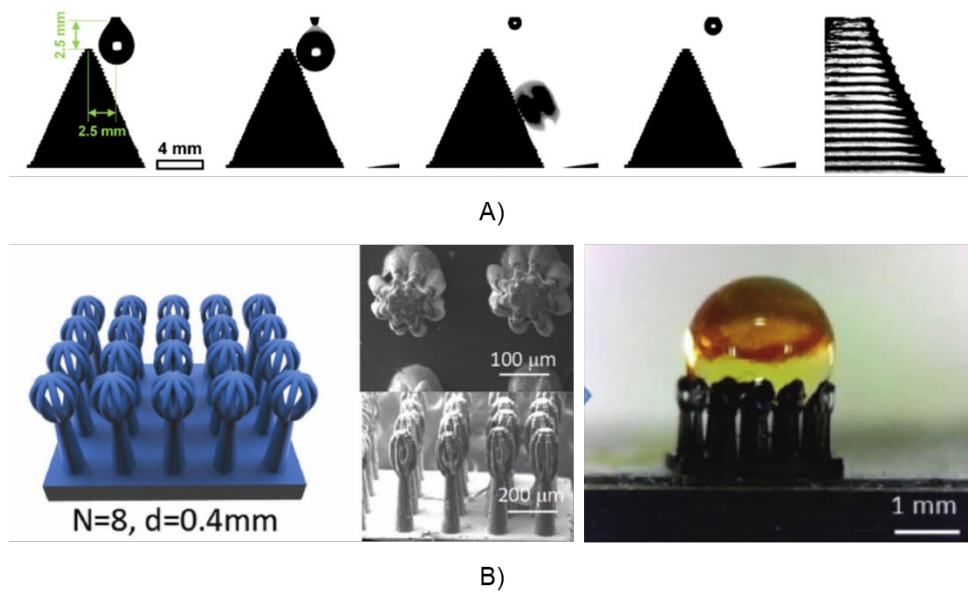


575
576 Fig. 8. (a) Honeycomb spacers to reduce fouling and improve flux [26], (b) Turbopromoters
577 reducing scaling and cake layer formations [50]. Reprinted with permission.

578
579 **3.1.2 Designing Superhydrophobic Membrane Surfaces**

580 Mechanical features and patterns to increase the roughness of membranes can be designed into
581 the surface at the sub-micron level without the need for further surface chemical coatings and
582 modifications. This represents a paradigm shift away from employing chemicals with inherent
583 hydrophobic properties that prevent wetting, limit fouling, and improve fluxes. Kang et al.
584 [129] developed a hydrophobic surface with a contact angle of $\sim 143^\circ$ and a surface roughness
585 of $36.42 \mu\text{m}$ (Fig. 9). The surface demonstrated a rolling-off phenomenon, supporting the use
586 of current 3D printing technologies for future scaled production of hydrophobic components.

587 The design and fabrication of 3D printed superhydrophobic surfaces into membranes could
 588 reduce biofouling for membrane distillation processes, leading to prolonged flux improvements
 589 and lower performance decline over time. Different superhydrophobic features could be
 590 designed into the membrane's surface that can lead to highly optimal and beneficial properties.
 591 By altering these features, membrane designers can experiment and develop membranes with
 592 the right properties for commercial applications.



593
 594 Fig. 9: Images showing the hydrophobic properties of 3D printed surfaces applicable to water
 595 treatment and desalination (a) FDM 3D printed micro-pyramids showing hydrophobic
 596 patterns and performance [129], (b) 3D printed microstructures mimicking the
 597 superhydrophobic properties of the *S. Molesta* leaf [130]. Reprinted with permission.

598

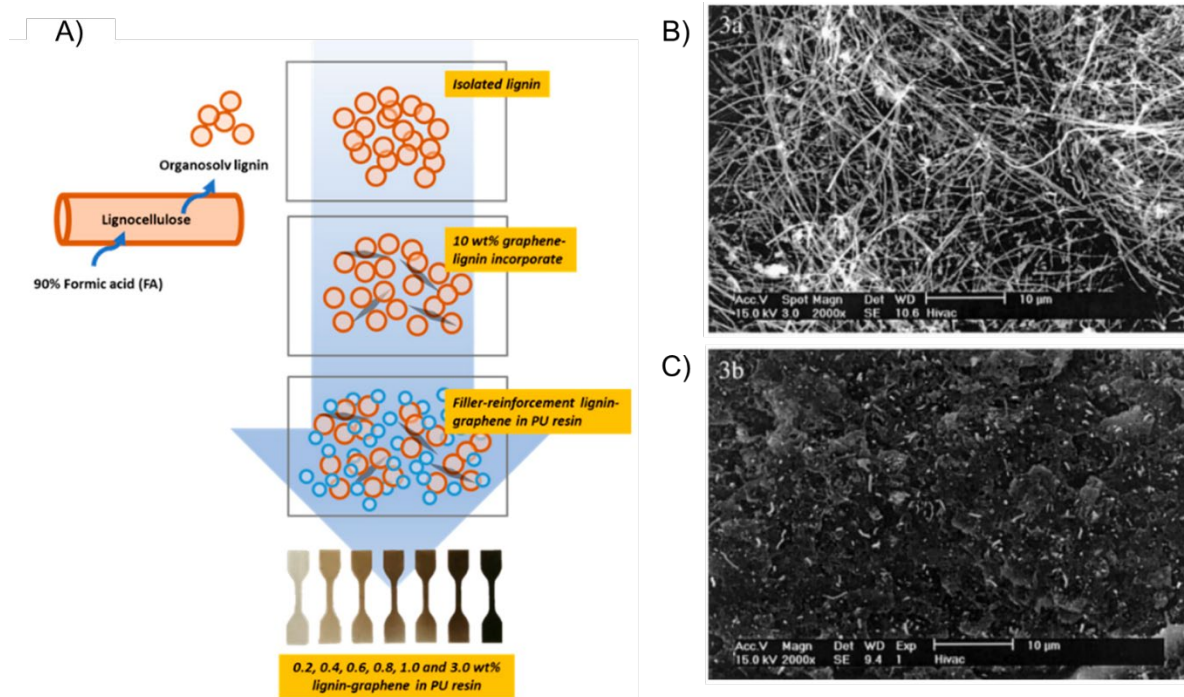
599 **3.1.3 3D Printing Nanofiber Reinforced and Composite Membranes**

600 The successful commercialisation of TFC membranes in the past could see a renewed path
 601 utilising 3D printing for composite membrane desalination. The combined use of different
 602 materials each serves a unique purpose in TFC membranes. With an active barrier layer to
 603 prevent the passageway for salt ions, a porous layer, and a support layer to improve membrane
 604 mechanical durability. Given a wide range of materials ranging from ceramics, polymers,

605 metallics, and other composites have been used to fabricate models, its applications towards
606 membrane manufacturing should not be overlooked. The benefits of multi-material printing of
607 nanofibrous and composite materials were realised in past studies [77] [80] [131] [132] [133]
608 where higher tensile strengths and hardness were found through composite 3D printing
609 materials. The proper mixing of this material was just as, if not, more important as the printing
610 conditions itself. Ensuring that uniform properties of the material would allow printed
611 components not to fail due to the presence of unwanted voids. Fibres could be printed within
612 membranes that improve its mechanical strength using both DLP and FDM technologies (Fig.
613 10), making the membrane more suitable for high-pressure RO applications. Rather than
614 printing supporting layers, fibrous supporting matrixes could be embedded within the
615 membranes, further reducing the overall thickness, and improving the manufacturing times by
616 simultaneously printing both supporting fibres and the membrane material. To date, multi-
617 material printing has been used in the areas of FDM-PLA [134], DLP-SLA [89] and inkjet
618 [135] [136] [137] printing. By combining multiple materials within 3D printing, membrane
619 compatibility [138], versatility [139], and durability [89] could all be improved, making 3D
620 printed membranes highly applicable and appropriate for more commercial desalination
621 applications.

622

623



624

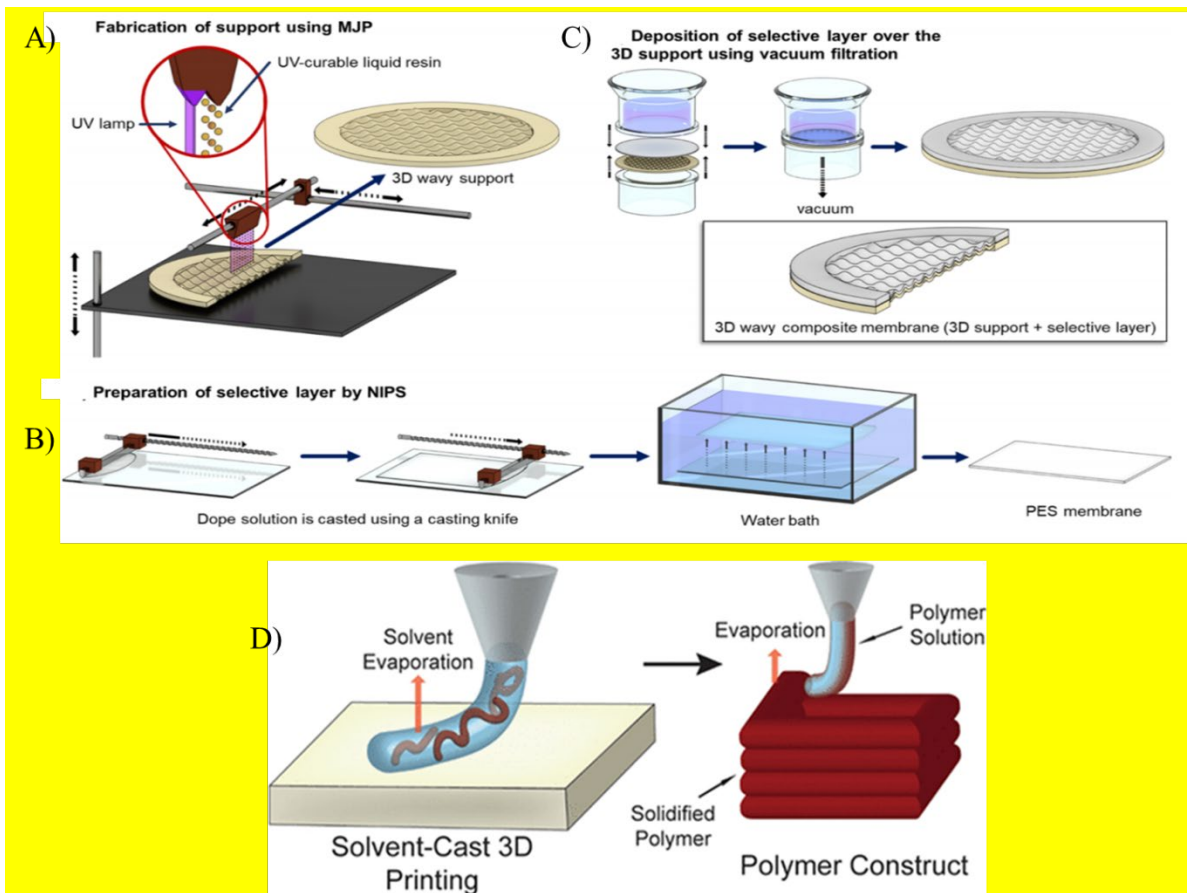
625

626 Fig. 10. (a) DLP printing with organosolv lignin fibres was used as reinforcement material
 627 with graphene nanoplatelets, improving tensile strengths by 27%, reprinted with permission
 628 [80]. (b) FDM fibres before printing that shows a lack of structure and (c) after printing,
 629 showing a clearer structure, reprinted with permission from [132].

630

631 In the manufacturing of conventional membranes such as symmetric, asymmetric, and
 632 composite TFC membranes, 3D printers can currently fabricate models consisting of more than
 633 one material for metals [140] and polymers [141]. With asymmetric and composite membranes
 634 consisting of a dense, porous, selective, and mechanical support layer, 3D printers can use
 635 multiple nozzle heads or resins to print different layers of distinct material for a single model.
 636 Mazinani et al. [142] and Al-Shimmery et al. [57] 3D printed a support layer which was then
 637 superimposed with a selective layer, creating a wavy featured membrane which exhibited anti-
 638 fouling benefits and improved water permeability (Fig. 11 (a-c)). The issue with this design is
 639 the lack of rollability, which is standard to that of RO desalination plant modules. The use of

640 low-resolution 3D printers to fabricate support layers is currently feasible, however, there lies
641 the limitation of scaling up the entire process and developing high resolution printing materials
642 that can endure 3- to 5-year operating conditions found in RO desalination processes. Thin film
643 layers have also been experimented with the use of PLA plastic suspended within a solvent
644 which will later evaporate to leave a film, known as solvent-cast printing (Fig. 11 (d)) [143].
645 The advantage of solvent-cast printing is that high resolutions can be achieved and expands the
646 range of polymers usable for 3D printing. However, solvent-cast printing is a recent
647 development and further studies into understanding the fluid drop mechanics, moderation of
648 the evaporation process, development of rapidly solidifying solvents, and creation of dedicated
649 composite thin film systems are all needed. It becomes possible to print symmetric,
650 asymmetric, and composite membranes using these 3D printing technologies in the foreseeable
651 future.



652

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

658

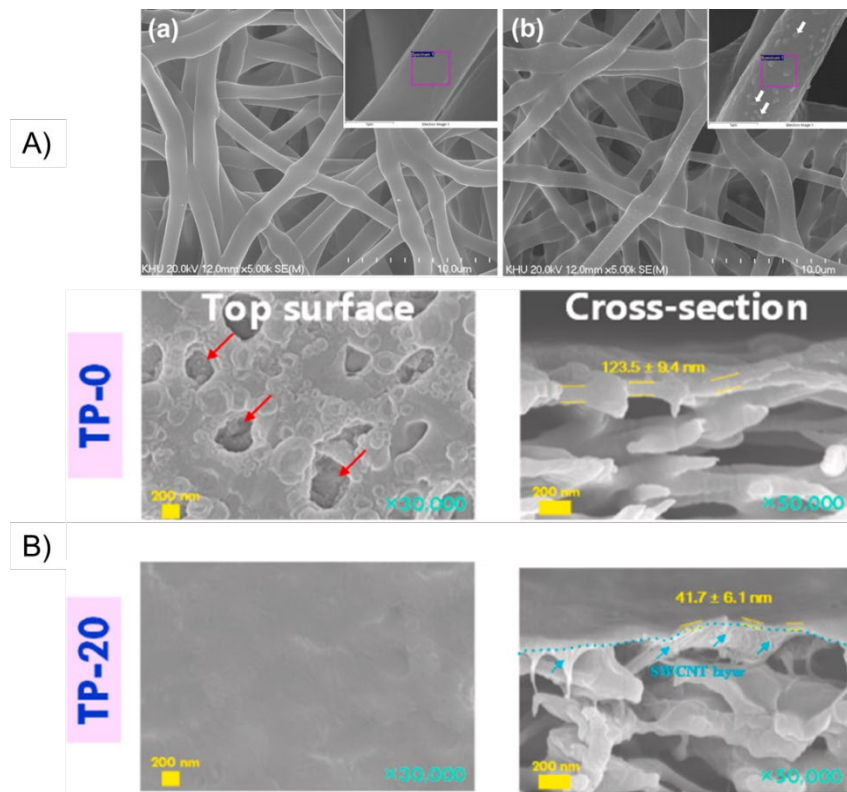
659 *3.1.4 Nanoparticles for 3D Printed Surface Coatings and Embedding*

660

661 Using inkjet printing, Ngo and Chun [144] produced surface coatings with superhydrophobic
662 properties using regular laser printers. While office printers are a mature and well-established
663 technology, its applications through membrane modifications towards water treatment and
664 desalination has been recent, particularly in the use of nanoparticles and materials such as
665 graphene oxide, silver (Ag) (Fig. 12(a)), and carbon nanotubes (Fig. 12(b)) [135] [136] [137]
666 [145] . Embedding nanoparticles within 3D printer materials enhances properties that would
667 otherwise not be possible when used purely on its own. With this application, the uniform
668 distribution of nanoparticles within the 3D printed polymers for membrane fabrication is an
669 area of promising application that removes the additional procedures taken for uniform
670 distribution within membrane active layers. Pawar et al. [146] reduced the curing times and
671 prevented the need for harmful solvents by using 2,4,6-trimethylbenzoyl-diphenylphosphine
672 oxide as the nanoparticle additive to the UV-curable inkjet solution. The environmental impacts
673 in the form of reduced harmful chemical usage and faster curing times (translating to lower
674 energy consumption) were achieved through this technology. Similarly, for membranes and
675 membrane components fabrication, the benefits could be realised when nanoparticle additives
676 can speed up production times and improve other properties without further post-treatment.
677 Addition of nanofillers enhanced the mechanical strength of 3D printed parts for another study

678 [147] using FDM printing, where tensile and flexural strengths respectively improved by
679 25.7% and 17.1%, with similar compressive strength improvements observed for ceramic
680 materials [148]. Therefore, a range of factors can be affected such as the membrane's
681 permeability, selectivity, hydrophobicity, hydrophilicity, conductivity, mechanical strength,
682 thermal stability, and anti-microbial properties [149] when utilising nanoparticles and
683 nanofibers in the development of membranes for water treatment and desalination. Though, its
684 uses in water treatment and highly septic environments teaming with microbial activity might
685 see more suitable applications where biofouling poses a more severe problem compared to that
686 of seawater. Depending on the type of water treatment technology, the materials of
687 nanoparticles used should be compatible with and be used to improve the performance
688 characteristics of the membrane. For example, the imparting of hydrophilic nanoparticles for
689 FO and RO membrane, and hydrophobic nanoparticles for MD. The bondage between the
690 nanoparticles and the polymeric medium should also be strong enough such that these particles
691 do not leak out into the solutions as previous studies have observed [150] [151], nor induce
692 undesirable characteristics leading to lower thermal stability [152].

693



694

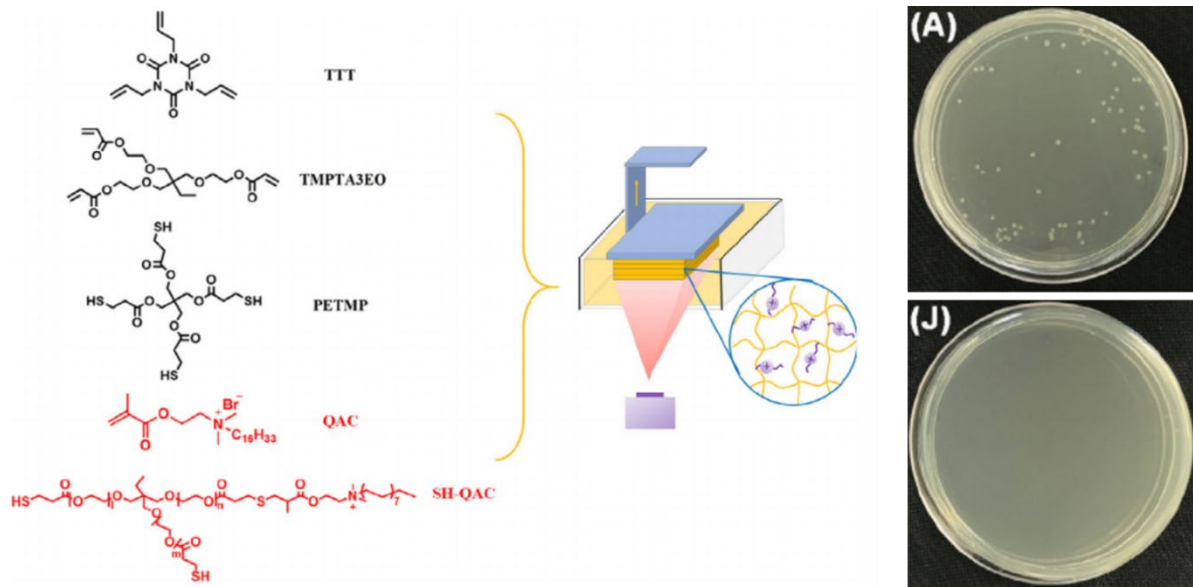
695 Fig. 12. (a) Embedded silver nanoparticles inhibited the growth of pathogens and water borne
 696 diseases [136], (b) polyamide active layer and pore sizes were both reduced from single-walled
 697 carbon nanotube coatings [145]. Reprinted with permission.

698

699 3.1.5 3D Printed Biofouling Resilient Membranes

700 3D printing can accommodate a range of materials with properties that resist the growth of
 701 bacteria and viruses on the surface of the part. Currently, DLP printing technologies have
 702 explored the use of mixed matrix resins with anti-microbial properties [153] [154]. With DLP
 703 3D printing, membranes fabricated with antimicrobial properties with this technology could
 704 have the potential of outperforming existing membranes with antimicrobial TFCs (Fig. (13)).
 705 The antibacterial rate for these resins was shown to be 100% [153] compared with other works
 706 in membrane literature that showed an antibacterial effectiveness of around ~80% [155] [156]
 707 [157]. Therefore, future developments in antimicrobial 3D printed membranes might pave way
 708 for membranes with highly effective antifouling properties, however, the issue of scaling may

709 present itself as an entirely separate problem. Because of this inherent antimicrobial nature of
 710 the membranes, the addition of pre-treatment chemicals within the water supply may not be
 711 necessary in some cases, saving further operating expenditure costs on chemical purchases and
 712 consumption, while preserving membranes in the absence of reagents and chemicals.



713
 714 Fig. 13. DLP 3D printed quaternary ammonium salt with methacrylate used to eliminate
 715 microbial growth from the surface of the photopolymer resin, with (A) showing *Escherichia*
 716 *coli* with no quaternary ammonium salt-type antibacterial agents. While (J) shows no bacterial
 717 growth after inoculating the 3D printing resin with 8% concentration of the antibacterial agent.
 718 Reprinted with permission from [153].

719

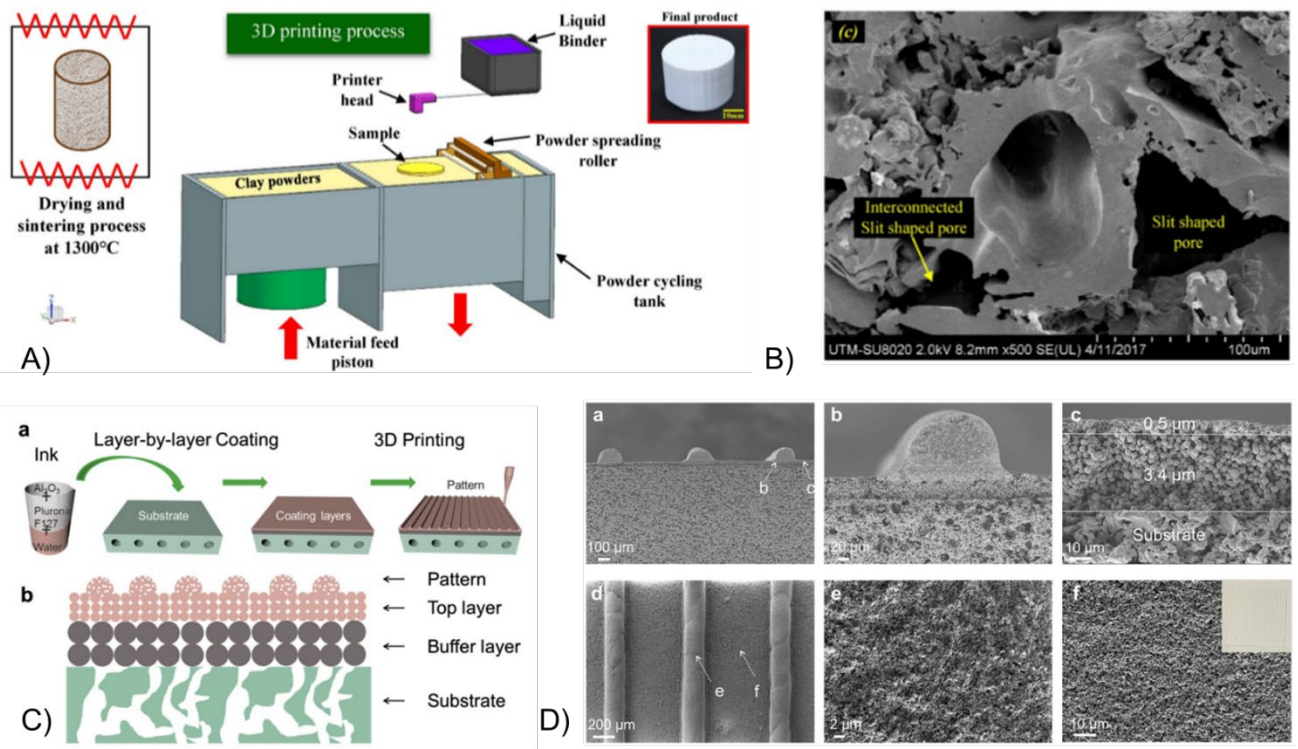
720 3.1.6 Ceramic 3D Printed Membranes for Pretreatment Systems

721 Currently, it is possible to 3D print microfiltration (MF) [158] [159] and ultrafiltration (UF)
 722 [58] [160] membranes to enhance flux performance. SLS printed polymeric microfiltration
 723 membranes have been fabricated which provide opportunities to adjust rejection rates and
 724 fluxes by changing polymeric particle sizes and distributions [158]. Likewise, these MF
 725 membranes have achieved rejection rates greater than 90% [158] [159]. Meanwhile, ceramic
 726 materials can be fabricated for MF, and it is also used for membranes requiring smaller pore

727 sizes for ultrafiltration pretreatment. The use of Solvent-based Slurry Stereolithography (3S)
728 3D printing methods can also be applied to fabricate ceramic membranes. The key advantages
729 of developing ceramic membranes are its chemical inertness, designability for antifouling
730 features, mechanical strength, lower pollution on the environment, higher filtration fluxes,
731 stronger thermal resistance, longer membrane life, and better backwashing cleaning operations
732 using high-pressure water [161] [162] [163] [164]. The advantages of using ceramic as a filler
733 is its low cost, where ceramic materials like clay, kaolin, and fly ash could be printed cheaply
734 and quickly - costing as little as between \$0.07/kg to \$1/kg [165] [166] [167] and have complex
735 structures printed ranging from a few minutes to hours [36]. As opposed to 3D printing with
736 polymers where the membrane porosity of the plastics must be directly printed into, the
737 porosities generated by the voids between the powder particles are what define the pore sizes
738 within ceramic membranes. Therefore, adjustments to the powder particle sizes through grind
739 milling, can be done to modify pore sizes and the porosity of the membrane. The rise in the
740 adoption of ceramic 3D printed membranes will increase the compatible availability of
741 chemicals used for pretreatment desalination plants, potentially reduce ongoing costs of
742 membrane replacements due to high backwashing efficiencies and longer membrane operating
743 lifespans, and lead to greater overall prolonged reduction in membrane fouling and scaling.
744 However, the high costs are more likely to come from the time it takes to sinter the membranes,
745 and the energy consumed during the sintering process, which can all be mitigated through
746 manufacturing at an economy of scale. Fig. (14) shows the various works that have
747 experimented the use of 3D printing for ceramic membranes.

748

749



750

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

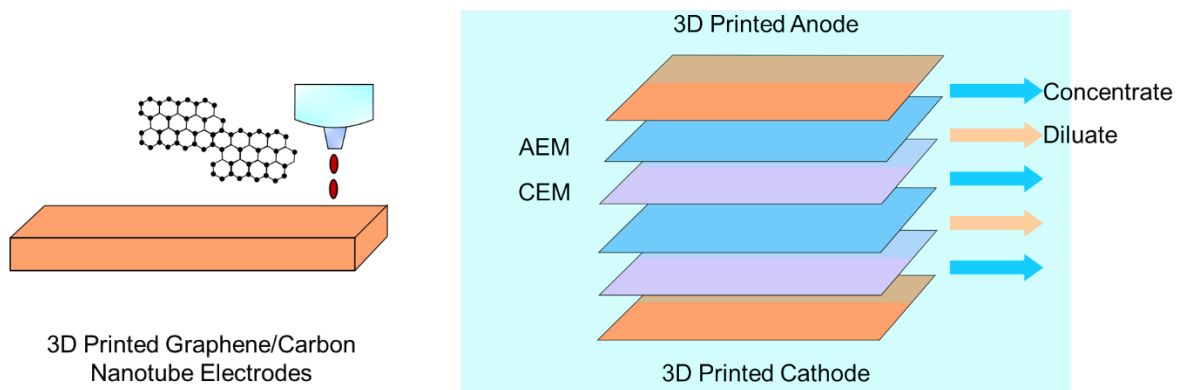
755

756 **3.1.7 3D Printed Electrodes for Brackish Water and Post-treatment Desalination Using**
 757 **Membrane Capacitive Deionisation**

758

759 Recent advances in 3D printing have been applied to the fabrication of electrodes using
 760 nitrogen-doped graphene oxide/carbon nanotubes (GO/CNT) as the material [168]. This led to
 761 electrodes with more cycle times and higher durability, with salt removal capacities of 75 mg/g,
 762 and improved energy recoveries of up to 27% [168]. Membrane capacitive deionisation using
 763 metal oxide CNTs has been experimented resulting in salt absorption capacities of 6.5 mg/g
 764 and a salt removal efficiency of 86% [169]. Combined with the CNT fibres which can be made
 765 continuously, the scalability of 3D printed CNT electrodes provides enormous opportunities

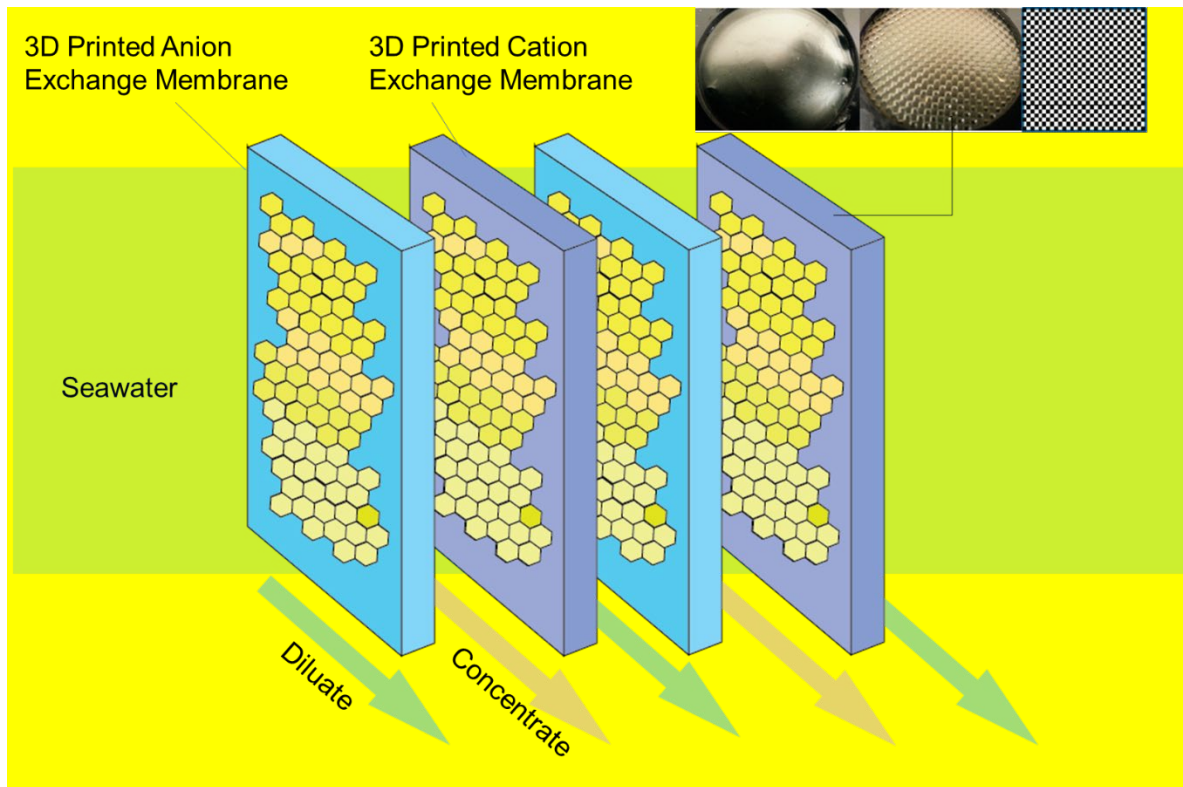
766 for industrial applications in the RO desalination industry. The improved energy recovery rates
 767 and the longevity of 3D printed electrodes would reduce the energy consumption of the overall
 768 RO plant when fed back into the system, and lower electrode replacement costs and
 769 frequencies. Therefore, 3D printed electrodes (Fig. (15)) can address a significant barrier that
 770 RO plants currently face – its high energy intensity. Similarly, other studies have used graphene
 771 combined with CNTs as electrode material [170] [171] [172] [173], where these studies have
 772 reported improved: strengths, electrical resistances, longevity, porosities, and power generation
 773 performance. 3D printed GO/CNTs could promise better performances compared to
 774 conventional electrodes from using various free-standing 3D printed structures that could
 775 drastically improve desalination performances, however, the application of 3D printed
 776 electrodes in water desalination is still currently in its early infancy stages. Currently,
 777 capacitive deionisation has applications in post-treatment of industrial brine and zero liquid
 778 discharge systems [174], bromide removal [175] [176], and selective removal of valuable
 779 metals and nutrients [177].



780
 781 Fig. 15. 3D printing applied to the fabrication of highly durable electrodes for salinity gradient
 782 power generation in RO plants.

784 **3.1.8 3D Printed Electrodialysis Exchange Membranes for Brine Treatment and Water**
 785 **Recovery**

786 The use of electrodialysis (ED) technology to treat RO brine has been done in previous studies
787 [178] [179] [180] [181] [182] [183] [184]. However, it was only recently that 3D printing
788 technologies were used to fabricate membranes for electrodialysis [185] [186]. Seo et al.
789 fabricated patterned exchange membranes for electrodialysis that showed lower ionic
790 resistances, which holds the promising potential to improving the performance of ED
791 membranes in the treatment of saline solutions, particularly in energy recovery by harnessing
792 salinity gradient power (Fig. (16)). Limiting current densities have been improved by 21%
793 through 3D printing of complex frames for improving the flow of ED streams, leading to
794 improved desalination performances and lower costs [187]. When applied to the post-treatment
795 of brine from RO plants, the possibilities for ED to improve water recoveries is immense, with
796 particular relevance to recent studies covering ED for RO zero liquid discharge systems [188]
797 [189] [190]. Water recoveries between 77% [189] to 85% [191] were achieved with brine
798 salinities as high as 125 g/L being concentrated [189], while even higher concentrations from
799 70 to 245 g/L was attained with ED post-treatment brine concentration [192]. With the
800 incorporation of 3D printed ED patterned membranes, better energy recovery percentages and
801 desalination performances could be realised given the potential for higher limiting current
802 densities and lower ionic membrane resistances, with positive impacts on the environment
803 where brine is no longer discharged into the ocean when 3D printed patterned post-treatment
804 ED membranes are used for RO brine concentration and zero liquid discharge.



805

806 Fig. 16. 3D printed pattern exchange electro dialysis membranes for desalination. Adapted from

807 [185].

808

809 **2.1.9 Surface Functional Groups**

810 Some studies have examined surface functional properties for 3D printing plastic covalent
 811 bonding strengths via modifications. Several surface modifications methods to strengthen
 812 covalent bonding include alkaline surface hydrolysis, atom transfer polymerization,
 813 photografting by UV light, plasma treatment, and chemical treatments after plasma treatment
 814 [193] [194]. Various studies for example have used dopamine [195] [196] [197], alkaline
 815 hydrolysis [198], and surface entrapment with chitosan [199] to modify surfaces for 3D
 816 printable plastics to serve as adherent platforms for post-modification with additional materials.
 817 These studies have shown successful bonding strengths between the chemicals after surface
 818 modification was completed. Surface modifications using metals have been shown to yield
 819 greater strengths [200] and fatigue endurances [201]. However, there are still challenges

820 required for this to be realised, one being the study of sturdy and durable surface functional
821 layers on a variety of different substrates [194] that are required to produce successful and
822 commercially viable membranes through 3D printing. These studies show the affinity that 3D
823 printing materials have towards successful surface modifications that will help make 3D
824 printed membranes highly comparable to that of conventionally fabricated membranes.
825 Currently, DIW printing is helping to achieve this.

826

827 *3.2 3D Printing Infrastructure for Desalination Plants*

828

829 While 3D printing for membranes is confined at the micro scale, in applications where
830 resolution is not an issue, the fabrication of structures through 3D printing onsite can help
831 reduce the engineering and procurement costs (EPC) of desalination plants. This will
832 significantly reduce EPC costs by printing components onsite, therefore, reducing construction
833 and logistical costs on the project. The advantages of applying 3D printing for construction
834 were cited to reduce time and costs, improve the level of customisability, higher sustainability,
835 reduce material consumption, and increase the safety of work [48] [202] [203] [204]. In line
836 with previous 3D printing works, the price of 3D printing infrastructure goes down the more
837 recycled aggregate was used [64], however, the environmental impact is much larger than that
838 of cast-in-situ concrete when raw unrecycled cement is used in the mix to maintain the strong
839 foundations required [205]. The challenges for the use of 3D printing concrete structures are
840 the right mix of plasticisers and silica, with too high of a viscosity leading to improper extrusion
841 with the right mechanical strengths [202]. The material mixture barriers and the significant
842 environmental impact that 3D printing infrastructures can have is still a recent area for further
843 investigation. While the benefits for greater customisation and recyclability of materials are
844 obvious, the potential to significantly reduce the EPC of desalination plants should not be

845 overlooked. Although the need for complex architectural designs is absent in desalination
846 plants, the primary incentive for its application are the reduced construction costs and greater
847 potential for sustainable production for all the required different plant assets.

848

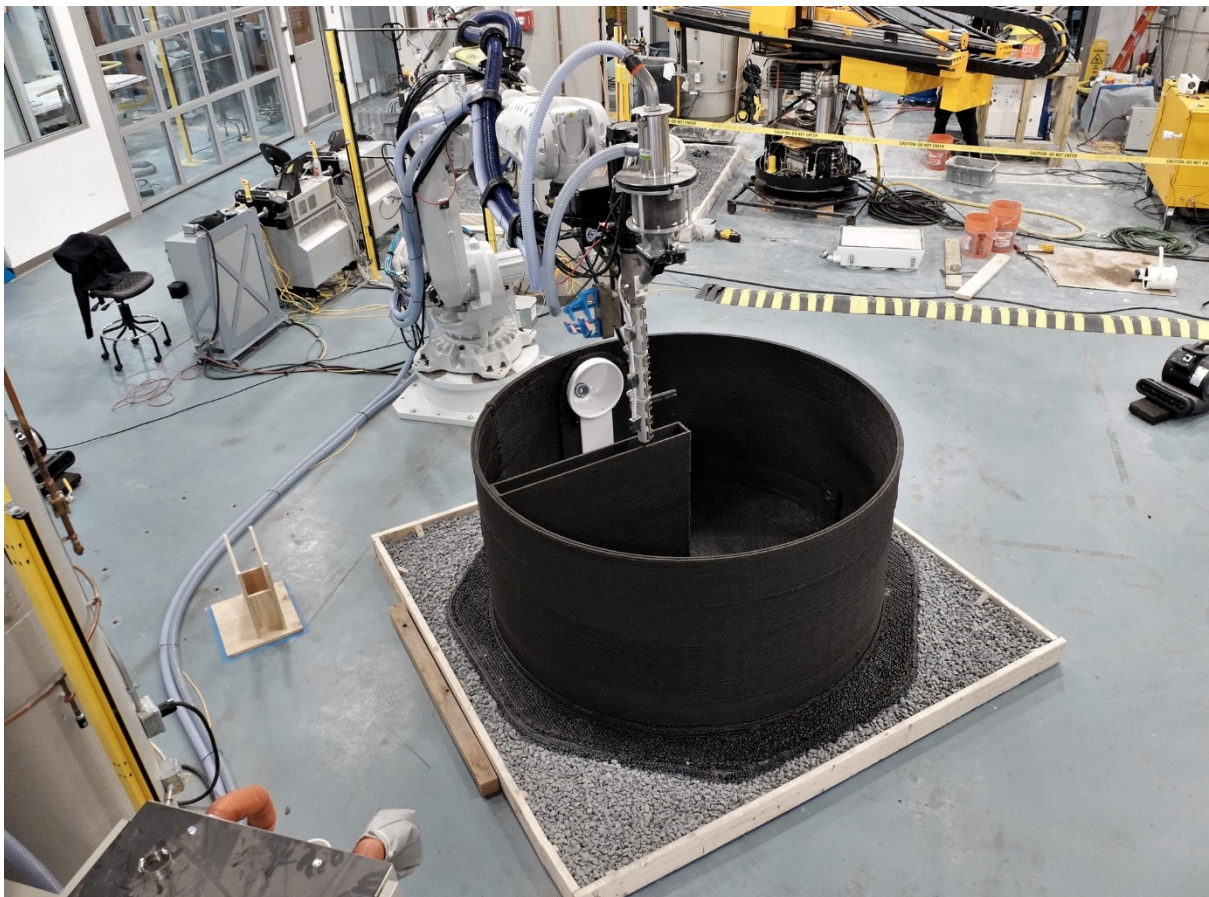
849 ***3.2.1 Desalination Buildings and Water Tanks***

850

851 3D printing of buildings on desalination plant sites will lead to environmental and procurement
852 cost savings. This is a new area of research that is currently still being studied with limitations
853 confined to the selection of structurally sound materials. The main benefits for the 3D printing
854 of buildings are the improved safety, cost reductions through improved construction methods
855 such as “Contour Crafting” and D-Shaped printing, and reduced pollution on the environment
856 [48] [203] [206]. The reduced labour and framework costs resulting from automated 3D
857 printing of construction materials will be a strong focal point for interested desalination plant
858 operators [205]. However, the use of concrete directly for 3D printing will have a higher
859 negative environmental impact compared with conventional in-situ techniques [205]. In future
860 applications of 3D printing for infrastructures, particularly for desalination plants, the selection
861 of materials that are more sustainable and structurally sound is needed to make the technology
862 more advantageous over conventional construction. Another main advantage is the
863 construction of irregular building shapes, a benefit desalination plants will find irrelevant.
864 However, irregular designs may see more practical use when desalination plants are located
865 within harsh terrain that make it logistically difficult to suffice construction work. Currently,
866 3D printing for infrastructure is confined to small scale buildings as opposed to large-scale
867 ones such as skyscrapers [206]. Because multi-story buildings are rarely ever used for
868 desalination plants, making 3D printing highly compatible. Solutions such as pre-fabrication
869 of buildings, changing designs as it is made, and optimising the infrastructure according to

870 unique operating and design conditions, are some other benefits that 3DCP could have. Current
871 limitations include printing overhanging structures, non-standardised concrete testing for
872 mechanical strength, the need for reinforcement in some areas, and consistent mechanical
873 integrity [207]. Mesh reinforcing methods combined with 3D printing were applied to work
874 around the issues of low mechanical strength for concrete structures by embedding steel rods
875 before and after printing [208]. Similarly, water storage tanks (Fig. 17) can also be fabricated
876 alongside 3D printed buildings, producing all of the necessary infrastructure needs through one
877 printing platform.

878



879

880 Fig. 17. 3D printed water storage tank from Teslarati [209].

881

882

883

884 *3.2.2 Pipelines*

885

886 3D printing of pipes is an emerging field currently limited by its weak interlayer bonding
887 strengths [210]. Zhang et al. [210] proposed printing according to the axial strengths being
888 applied that would enhance the end product's mechanical strength. While path planning
889 provides a greater degree of freedom to design pipes, they lack the mechanical strengths that
890 are acceptable for high-pressure desalination processes. Other studies have used methods such
891 as changing the print paths to enhance the pipe's surface quality [211] [212] [213] [214]. Future
892 3D printed pipes will have both the freedom of producing entire pipelines that are also
893 mechanically strong and versatile in design. Currently, some computer aided design (CAD)
894 software can automatically generate pipes, which reduces time and cost on both production and
895 design engineering tasks.

896

897 Meanwhile, recent advancements in 3D printing technologies make it possible to print sensors
898 directly into pipelines during manufacturing [215]. This allows easy identification and
899 monitoring of the pipe's conditions throughout the lifetime of the plant, while protecting the
900 sensor from the harsh seaside environments – paving way for predictive maintenance solutions
901 and the use of digital twins [216] [217]. This means that pipes can be stored underground and
902 monitored using this tagged sensor system, thereby reducing the overall footprint of the plant
903 when land scarcity is an issue. Integrating temperature and salinity sensors within the pipelines
904 could also be done using this technology, providing much more versatile options that would
905 support the digitisation of desalination plants that are increasingly gaining attention due to the
906 potential for reducing energy consumption [218] [219]. Therefore, embedding sensors within
907 pipelines allows for the complete integration of monitoring temperature and salinity conditions
908 with digitised desalination plants, reducing land usage and energy consumption.

909

910 *3.3 Components*

911 *3.3.1 3D Printing for Optimised Membrane Modules*

912

913 The advantages of using 3D printing are the ease of experimentation and optimisation of
914 membrane modules for a wide variety of emerging desalination technologies such as reverse
915 electro dialysis, FO and MD. Currently, the lack of module optimisations for MD [220] [221]
916 [222] are what drives up its costs. Meanwhile, another experiment has shown that the cost for
917 membrane modules was a barrier [223]. This lack of standardisation and labour intensity to
918 fabricate modules is a barrier in the experimentation and optimisation for more effective
919 emerging desalination systems.

920

921 For MD, thermal limitations and barriers must also be overcome, particularly in longer-termed
922 studies where feed temperatures as high as 80-90°C are used which can lead to warpage and
923 thermal creep within the printed modules. Promising applications for 3D printing lie in design
924 and optimisation of FO modules, given that the cost of FO membranes is among the highest
925 for FO and the absence of both thermal and hydraulic pressures involved improve 3D printing
926 applicability. For example, Linares et al. [224] conducted a sensitivity test and showed that
927 membrane modules contributed significantly to the FO plant costs.

928

929 Studies that have experimented with 3D printing to optimise performances using printed
930 spacers and modules were made. Frames and innovative features were printed for AGMD
931 modules in another which maximised the latent heat recovery from the solar-MD operation
932 [225]. This was achieved by varying the thicknesses of the frames which provided the air gap,
933 therefore improving the overall thermal efficiency of the solar-AGMD system. The use of

934 complex models such as helical baffles, otherwise impossible for conventional fabrication,
935 were used to recycle thermal energy, which reduced energy consumption by ~60%, and
936 improved the compactness of the overall VMD design [226]. Therefore, 3D printing provides
937 a myriad of opportunities towards improving the viability of MD systems by allowing complex
938 and intricate designs to be fabricated beyond the conventions of subtractive manufacturing
939 processes. Costs in experimenting with different parameters such as air gap widths, wall
940 thicknesses, materials, and surface properties using 3D printing, can greatly reduce the cost of
941 research and development for MD systems. Currently, MD is an emerging desalination
942 technology which can potentially have its commercialisation status expedited through greater
943 adoption of 3D printing for unconventional MD module designs, fabrication, and
944 experimentation. This commercial expedition, however, is not specifically limited to MD.

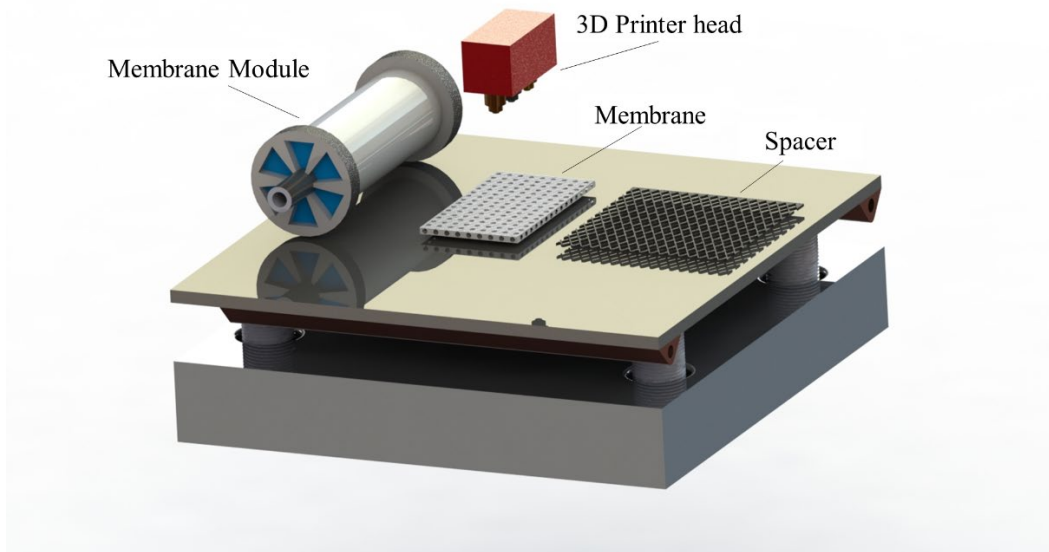
945

946 *3.3.2 Complete 3D Printing of Membranes, Modules, and Spacers*

947

948 It has been proposed that the fabrication of the entire membrane, spacer, and module all at the
949 same time will further cut down costs [39]. While this has not been performed yet, printers are
950 currently able to print with multiple materials, combining the fabrication of the entire
951 pretreatment system with ceramics and polymers for flexible manufacturing of entire
952 pretreatment cartridges. This simplifies the entire design and engineering process as opposed
953 to traditional manufacturing processes where membrane, spacer, and module fabrications have
954 been manufactured separately, requiring more complex logistical supply chains to deliver them
955 to a central location for assembly. The simplified complete printing of membranes, spacers,
956 and modules is visualised in Fig. (18).

957



958

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

961

962 ***3.3.3 Metal 3D Printing of Heat Pumps for MD Energy Recovery***

963

964 For heat pumps, the use of SLS technologies to produce unconventionally complex metal
965 shapes for highly efficient heat-transfer operations was also explored in other works [227]
966 [228] [229] [230] [231] [232] [233] [234]. Such uses could be applied in heat pumps for thermal
967 extraction from permeate streams and thermal recycling in MD desalination. These improved
968 thermal performances could also be used for MD thermal pumps in recovering latent heat from
969 permeate streams. Thermal recovery reduces wasted heat energy in MD setups and allows for
970 the further reduction in energy costs and consumption. Given most MD systems utilise low-
971 grade waste heat or renewable sources, the improved efficiencies lead to greater output for
972 lower input. The application for SLS metal printing technologies to MD heat recovery pumps
973 however, remains yet to be studied and shows promising future applications in advancing the
974 commercial viability for MD when complex heat sinks can be made to extract greater latent
975 heat from permeate water. The combined use of SLS for both pumps and heat absorbers provide

976 the benefits of improved thermal absorption from the permeate stream and thermal energy
977 storage for prolonging the use of solar-based MD systems well into the night. However, future
978 challenges for SLS printing for MD are the study of material properties in desalination settings
979 given that SLS materials and the resulting layered, structured models will differ in properties
980 against its unprinted form [235]. Further studies into SLS materials and its response within
981 desalination environments are needed before fully appreciating the benefits that SLS printing
982 would bring for heat sinks in MD heat-recovery pumps.

983

984 ***3.3.4 3D Printing for Enhanced Pump Maintenance, Performance, Manufacturing, and*** 985 ***Durability***

986

987 The use of polymers for 3D printing will see limited applications in membrane desalination
988 due to low mechanical strengths tolerating pressures of up to 400 kPa [236], with many current
989 applications confined to microfluidics [237] [238] [239]. Currently, limitations for 3D printing
990 polymer-based pumps are the high surface roughness and low mechanical strengths, therefore,
991 alternative non-polymer materials must be used for impellers and pumps. Wax patterns can be
992 3D printed and cast into metallic pumps which can then receive finishing operations to create
993 a smoother surface [240]. Laser metal deposition (LMD) uses a high-powered laser to melt
994 metallic powder which is carried by an inert gas [241]. Unlike other forms of 3D printing where
995 printing is confined vertically as seen in SLS or selective laser melting (SLM), LMD can create
996 parts in any direction and axis orientation [241] [242] and can expedite the fabrication time of
997 parts in any direction of geometry. The use of various alloys combined with hybrid
998 manufacturing also makes it possible to produce corrosion-resistant parts [243] [244] [245].
999 This corrosion resistance makes it possible for pumps to be used in environments with higher
1000 pH and salinity. Combined with hybrid manufacturing, pump refurbishment, and repair costs

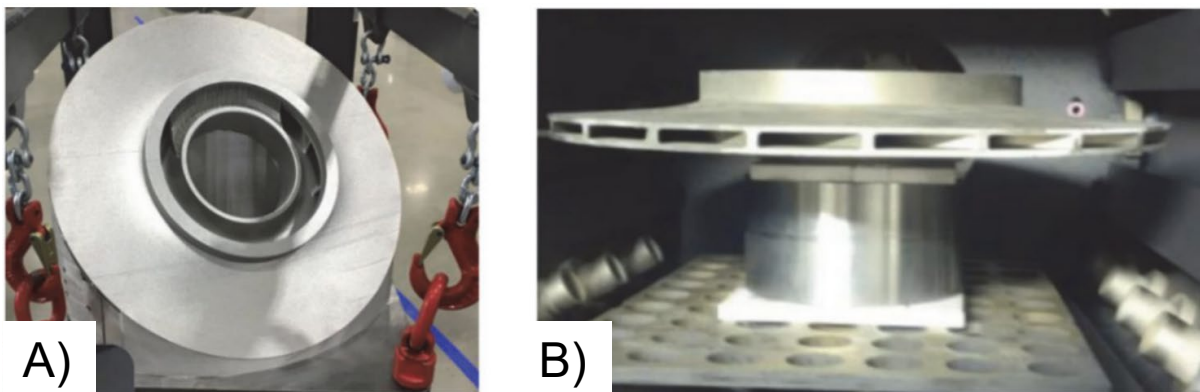
1001 will also be reduced for these advanced pumps [246] [247]. However, it is still currently unclear
1002 which alloys are the best used for the additive refurbishment process within pumps exposed to
1003 harsh environments, and further research is still needed in this area to better understand
1004 behaviours such as hydrolysis and corrosion reactions between 3D printed composite metallic
1005 alloys and seawater. One of the latest metals used in 3D printing for pumps - Inconel 718 (Fig.
1006 19) – enabled researchers to explore optimal impeller designs for pumps which can also be
1007 applied towards developing highly efficient energy recovery devices.

1008

1009 Pumps within desalination plants will operate under harsh conditions, safeguarded by metallic
1010 alloys that are resistant to corrosion, maintained and easily repaired through combined
1011 technologies that scan, identify issues, rapidly printed components for installation, and with
1012 newer and more advanced pumps that are optimised for different desalination operating
1013 conditions and environments without expensive retooling.

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1017 Fig. 19. Metal 3D printing with IN718 material taken from [248] through open access, (a)
1018 showing the final prototype of the metal impeller and (b) during the fabrication process Metal
1019 3D printing of pumping components will reduce manufacturing costs and time, contribute to
1020 cheaper desalination plants, and improved maintenance, and operating life of pumps.

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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] [253] [254] [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 1,000 mg/L of salt concentration increase, an added 0.76 bar is applied to RO pumps [256]. For standard RO, this is between 50 to 70 bar [257] [258]. For seawater intake pumps, this pressure is substantially lower - between ~2 - 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 exposure to lower operating pressures.

1037 Table 4: Recent applications of 3D printing towards additive manufacturing pump components.

3D Printing Technology	Pumping Component	Remarks	Source
FDM	Impeller	FDM cost 40€ and 3 hrs, 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 hrs manufacturing time using additive-3D printing (with conventional PLA), compared to 10 hrs 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 CO ₂ , 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]

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1039 The freedom to customise and print new membranes using Inkjet printing shows the most
1040 promising outlook and solves the challenge confining 3D printers to the small range of
1041 materials that can be used for water desalination. The sub-micron resolutions that 3D printing
1042 provides allow for the design of hydrophobic surfaces on the surface of membranes, further
1043 enhanced with surface coatings that make membranes ideal for MD applications and having
1044 anti-fouling properties. While mass-customisation and optimisation of spacers and modules
1045 reduce the cost on membrane researchers to design and test unique module and spacers for the
1046 best setup in each of the desalination technologies, while allowing new and optimal
1047 components to function best by changing its design features depending on the operating
1048 conditions of the desalination plant. Lastly, while 3D printing has been synonymous with sub-
1049 micron resolutions and the production of custom small parts, at much larger resolutions, 3D
1050 printing can yield environmental and EPC advantages when designing and constructing entire
1051 desalination plants. Although components such as pipes and water storage tanks are standard
1052 components and the printing of modules able to withstand high pressures is far off, custom
1053 buildings particularly in difficult to reach regions may benefit from the use of 3D printing for
1054 infrastructures.

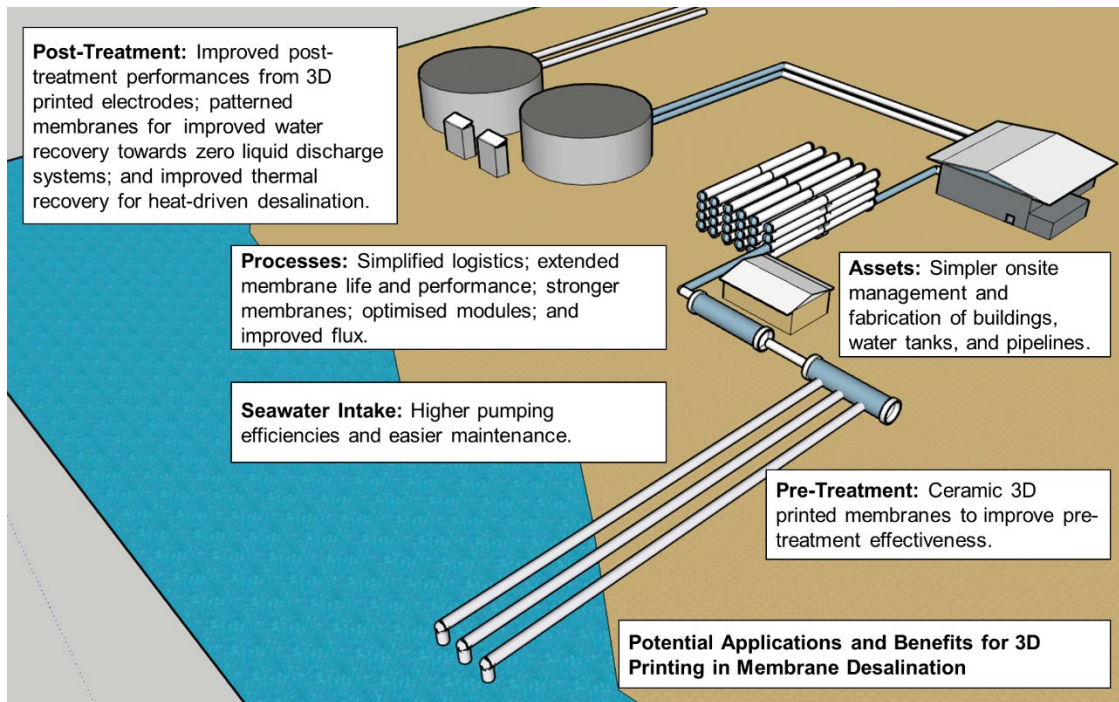
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1056 3D printing is still an emerging state of technology despite its origins tracing back to the mid-
1057 1980s. According to Gartner's hype cycle examination of 3D printing technologies [268],
1058 nanoscale 3D printing could see commercial success within the next 10 years, while
1059 stereolithography, binder jetting, and material extrusion methods can take between 2 to 5 years
1060 to become commercially successful [268]. The most well-established sectors for 3D printing
1061 are its services provision and model creation software. The advanced development of 3D
1062 printing software can help simplify the design, conversion, and fabrication of much more
1063 complex membranes at the nanometre scale without having to create and modify large files.

1064 Meanwhile, there is yet to develop a software which specifically designs and optimises
1065 desalination components that could easily be transferred to the printer for fabrication.
1066 Nevertheless, 3D printing research today yields promising potentials towards simplifying the
1067 manufacturing of complex membrane desalination components and logistics networks
1068 surrounding desalination plants.

1069

1070 This review paper explores the potential applications for 3D printing technologies in other parts
1071 of the desalination plant from spacers, modules, membranes, and infrastructure 3D printing. It
1072 is posited that 3D printing application for desalination will promote the digitisation of plants,
1073 improve the efficiency of desalination processes, contribute to more sustainable construction
1074 and manufacturing processes, and help aid in the reduction of energy consumed for
1075 desalination. These solutions offered by 3D printing can make desalination more widely
1076 accessible to communities particularly those in developing countries who lack access to basic
1077 infrastructure, where small-scale plants could potentially be 3D printed on the spot and also
1078 have spare sparts fabricated at the exact same location. Although, 3D printing for desalination
1079 is still in its infancy, currently there is growing interest in its applications towards desalination.
1080 As the world's water scarcity becomes more severe by the day, 3D printing technologies may
1081 be the answer to the world's water shortage problems. These points are visually summarised in
1082 Fig. (20).



1083

1084 Fig. 20. Overall benefits of 3D printing and its potential future applications and benefits for
 1085 the entire system.

1086

1087 **4.0 Conclusions**

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1089 3D printing technologies open up a world of opportunities in the design, customisation,
 1090 development, testing, and exploration of newer and improved membranes and its associated
 1091 components for commercial use. This review has addressed inherent limitations of current 3D
 1092 printing materials and technologies with membrane water desalination. The use of 3D printing
 1093 currently sees higher potential for spacers and membranes than modules. This is because
 1094 presently, there is very little desalination studies done solely on the performance of 3D printed
 1095 membrane modules, however, 3D printed modules can help expedite the commercial viability
 1096 of emerging membrane desalination technologies by reducing experimental costs and the
 1097 exploration of unconventional designs. While DLP and CLIP show a more promising outlook
 1098 in the fabrication of membranes mainly due to the higher resolutions and continuous production

1099 capabilities for membrane production scalability. It is estimated that by 2030, the cost of 3D
1100 printing will be reduced by between 50-75% on a BVUC basis, however, limitations in terms
1101 of scalability and resolutions will hinder its adoption in membrane fabrication. Future
1102 perspectives are provided on the applicability of 3D printing for membrane desalination plants
1103 across membranes, spacers, modules, and plant assets. Thanks to the wide-ranging benefits 3D
1104 printing will bring, opportunities to design and optimise desalination plants across multiple
1105 levels are vastly expanded. Due to these benefits, 3D printing has the potential to help tackle
1106 water problems across the world.

1107

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