3D printing for membrane separation, desalination and water treatment

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Abstract

Additive manufacturing or commonly known as 3D printing is driving innovation in many industries and academic research including the water resource sector. The capability of 3D printing to fabricate complex objects in a fast and cost-effective manner makes it highly desirable over conventional manufacturing processes. Recent years have seen a rapid increase in research using 3D printing for membrane separation, desalination and water purification applications, potentially revolutionizing this field. This review focuses on recent advancements in 3D-printed materials and methods for water-related applications including developments in module spacers, novel filtration and desalination membranes, adsorbents, water remediation, solar steam generation materials, catalysis, etc. The emergence of new 3D printers with higher printing resolution, better efficiency, faster speed, and wider material applicability has garnered more interest and can potentially reshape research and development in this field. The promising potential, challenges and future prospects of 3D printing, additive manufacturing, and materials for water resource and treatment-related applications are all discussed in this review.

Keywords: 3D printing; additive manufacturing; membrane; water purification; water treatment; desalination

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Abbreviation

3D	Three-dimensional
4D	Four-dimensional
ABS	Acrylonitrile butadiene styrene
AM	Additive manufacturing
BSA	Bovine serum albumin
CAD	Computer-aided design
CFD	Computational fluid dynamics
CLIP	Continuous liquid interface production
CNT	Carbon nanotube
DIW	Direct ink writing
DLP	Digital light processing
DMLS	Direct metal laser sintering
DOD	Drop-on-demand
EDTA	Ethylenediaminetetraacetic acid
EMB	Electron beam melting
EPS	Expanded polystyrene
FDM	Fused deposition modelling
FFF	Fused filament fabrication
FO	Forward osmosis
GO	Graphene oxide
HIPS	High-impact polysterene
LDPE	Low-density-polyethylene
LMH	Liter per square meter per hour
MB	Methylene blue
MBBR	Moving bed biofilm reactor

MD Membrane distillation
MF Microfiltration
MOF Metal organic framework
MPD M-phenylene diamine
NF Nanofiltration
NFC Nanofibrillated cellulose
NIPS Non-solvent induced phase separation
NP Nanoparticle
PA Polyamide
PBF Powder bed fusion
PC Polycarbonate
PDMS Polydimethylsiloxane
PEEK Polyether ether ketone
PES Polyethersulfone
PLA Polylactic acid
PP Polypropylene
PTFE Polytetrafluoroethylene
PVA Polyvinyl alcohol
PVDF Polyvinylidende fluoride
RO Reverse osmosis
SEM Scanning electron microscopy
SLA Stereolitography
SLM Selective laser melting
SLS Selective laser sintering
SSA Specific surface area
tCLP Transverse crossed layer of parallel
TEM Track-etched membrane
TFC Thin film composite
TMC Trimesoyl chloride
TPMS Triply periodic minimal surface
TPP Two-photon polymerization
UF Ultrafiltration
UV Ultraviolet
VOC Volatile organic compound
WHO World Health Organization
ZIF Zeolitic Imidazole Framework

1. Introduction

The development of new technologies and synthesis of new materials in the last four decades have propelled new frontiers and innovation in addressing a variety of environmental challenges [1]. One of the emerging and promising technological advancements is additive manufacturing or generally known as 3D printing, which is a layer-by-layer fabrication technique [2]. 3D printing can be used to fabricate objects with almost unlimited geometrical constraints, i.e., even complicated designs can be manufactured and assembled by a single pass [3]. This gives a clear advantage when compared with conventional formative manufacturing processes. The emergence of 3D printing technology has enabled rapid prototyping for various engineering and non-engineering applications utilizing a wide range of materials (e.g., polymeric, ceramic, metals, etc.) [4]. Recently, researchers have started looking at 3D-printed materials for membrane separation, water treatment and purification process applications. This stems from the issue of global water resource scarcity, which needs collaborative effort to provide sustainable solutions [5]. These solutions include applications of membrane technology (spacers, modules and membrane fabrication), solar absorbers/steam generation materials, sorbents for oil/water separation, materials for dye degradation and catalysis, etc. (see **Fig. 1**). One of the early applications of 3D printing was on module spacer design and development utilizing a net-design spacer for membrane separation [6]. Since then, different types of membrane spacer designs have been reported for applications such as reverse osmosis (RO), ultrafiltration (UF) [7], membrane distillation (MD) [8], forward osmosis (FO) [9], etc. There have been attempts on direct fabrication of 3D-printed polymeric [10] and ceramic [11] membranes, or as substrate to membranes [12]. However, due to resolution limitations, direct 3D printing of membranes is still a challenge. Recent developments in more capable 3D printers have addressed some of these limitations including multi-material adaptability. Some research groups have reported enhanced solar steam generation performance from 3D-printed materials, and for other uses such as in water remediation, wastewater treatment, and adsorption.

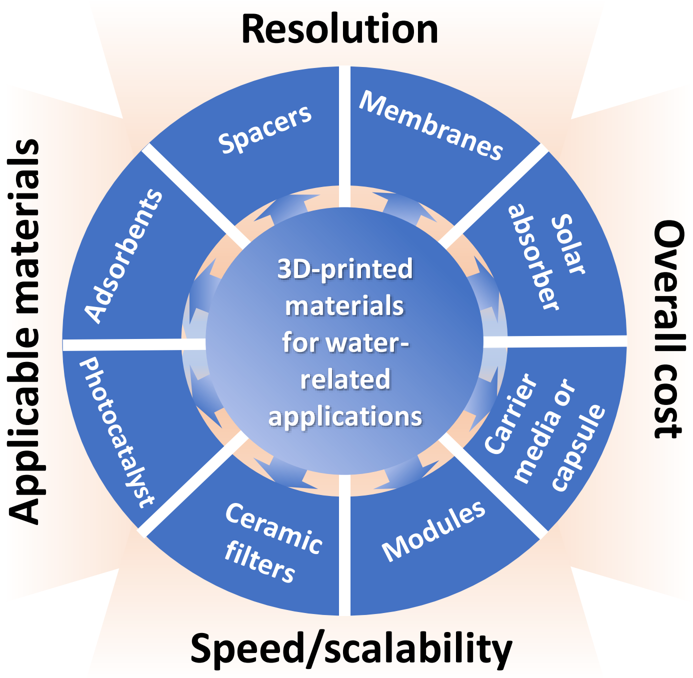

Figure 1. 3D printing has found its way to water-related applications. However, it still faces some issues on resolution, applicable materials, speed and scalability and the overall cost.

The past 10 years have seen a rapid increase in research and development on 3D printing for many applications as indicated by the exponential increase in publications over the years (see **Fig. 2**). Specifically, interest on 3D printing for water treatment/purification, and membrane separation applications has been growing recently as evidenced by the exponential growth of research studies and publications in the literature. From less than 20 articles published in 2010, papers related to 3D-printed materials for water-related applications have averaged around 300 papers published annually in the last 3.5 years alone. Clearly, research interest in this field is rapidly growing. Thus, there is a need to review, discuss and analyze recent updates of 3D-printed materials work and literature. A few review papers have attempted to provide new information in this regard, but are only limited to discussions specifically on membranes, or module spacers. Most published articles have been dedicated only on the discussion of 3D printing technologies and not their water-related applications [3, 13-15]. In this present review, we emphasize on the latest progress and developments of 3D-printed materials (polymeric and ceramic) with focus on applications for membrane separation, wastewater treatment, desalination and water purification especially those reported in the recent three years. Discussions include the design, fabrication techniques and performance of 3D-printed materials in water-related applications. General details about additive manufacturing, the materials used, techniques and related characterizations have also been included. The review concludes with the identification of challenges, and outlining of future prospects of 3D-printed materials for water-related applications.

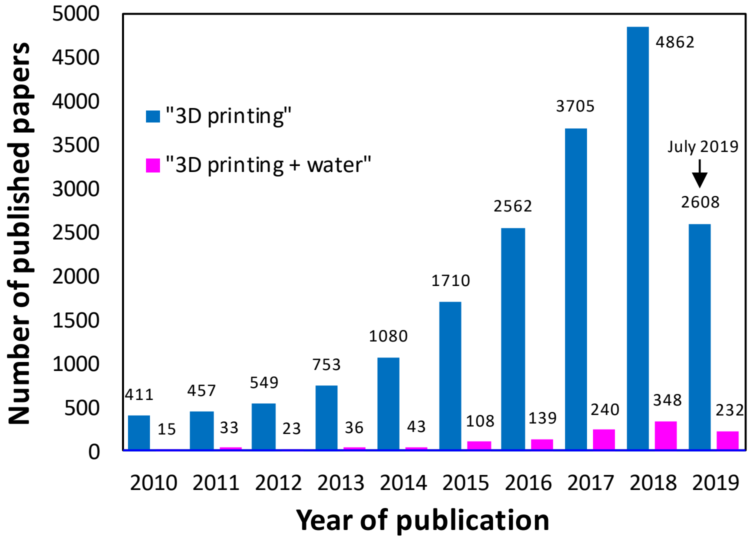

Figure 2. Number of publications related to 3D printing through the years (data are from Web of Science database with the keywords "3D printing" and "3D printing + water"). Search was refined to only include research and review articles in science and technology field.

2. Brief overview of additive manufacturing (3D printing)

2.1. Additive manufacturing process and techniques

Additive manufacturing (AM) or simply 3D printing is revolutionizing many fields of research and applications. Other terms associated with AM include rapid prototyping, layered manufacturing, direct digital manufacturing, additive fabrication, etc. In this paper, additive manufacturing and 3D printing are interchangeably used. Generally, "additive", indicates that the fabrication technique is based on printing or adding one layer at a time to produce the 3D structure based on a 3D computer aided design (CAD) model. **Figure 3** shows the general AM process flow. A 3D model of the desired design is first prepared, then subsequently converted to a 3D printer compatible file (usually .STL,.OBJ, or .AMF) [16]. The file is then processed using a slicing software/AM system (usually dedicated to a specific 3D printer), which slices the model in several hundreds or thousands of layers. Various parameters such as printing speed, layer height (resolution), infill, etc. are specified and optimized in the slicing process. The slicing process also converts the .STL file into a file type accepted by a particular 3D printer (G-code) [17]. The sliced file (G-code) is then transferred to the 3D printer, during which, the 3D printer can begin fabricating. After printing, the 3D-printed part usually requires post-processing to remove extra materials or stabilize curing (the extent of which depends on the printer type), and to prepare the part for the desired application [16].

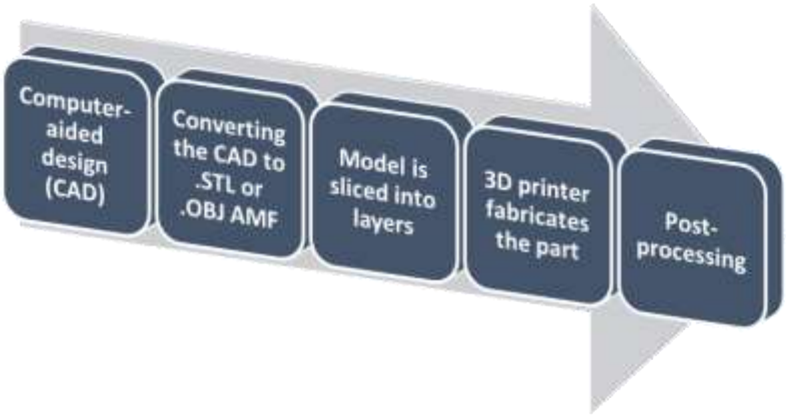

Figure 3. Schematic of the additive manufacturing (3D printing) process flow.

There are several 3D printing technologies available in the market and are mainly divided into the following categories [3, 13, 17-19] (although there are more):

1) Material Extrusion – fused filament fabrication (FFF), fused deposition modeling (FDM), Paste Extrusion
2) Powder Bed Fusion – selective laser sintering (SLS), for polymers; selective laser melting (SLM), direct metal laser sintering (DMLS), and electron beam melting (EBM) for metals
3) Vat Polymerization – stereolithography (SLA), digital light processing (DLP), two-photon polymerization (TPP) and continuous liquid interface production (CLIP)
4) Material Jetting – Polyjet, drop-on-demand (DOD)
5) Binder Jetting
6) Sheet Lamination

The most commonly-used 3D printers are the extrusion-based 3D printers, also known as FDM (see **Fig. 4a**) and filament freeform fabrication (FFF), which uses a thermoplastic filament as its printing material [20]. In FFF, the printer prints a 3D object by extruding a melt thermoplastic material following the sliced 3D model [18, 21, 22]. The melt material is positioned layer upon layer until the 3D object/part is created vertically. Stratasys has owned the patent for FDM since 1989 [23]. Common materials for FDM are polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), and recently, high performance polymers such as polyether ether ketone (PEEK) have also been used. This printing technique is relatively fast and inexpensive, but requires support structures especially for complex shapes [24]. The basic components of a typical FFF/FDM printer include the build platform, heated extrusion nozzle, and the filament material. Paste extrusion printing is similar to FFF/FDM wherein the material is extruded onto the build plate through a nozzle even at room temperature. This method can extrude a highly viscous material, which needs to become solid-like and maintain its shape after extrusion (thixotropic). Different types of materials may be printed including polymer resins, polymer solutions, gels, etc. Postprocessing is usually required [17].

Another common 3D printing technology is SLS additive manufacturing which is a type of powder bed fusion (PBF) process [22, 25]. **Figure 4b** shows a schematic of the SLS printing process. The components of this printing process include the build platform, the printing chamber (including the powder bed), powder reserve chamber (including the refilling powder), and the laser beam (source). The printing chamber and powder reserve chamber are initially heated to a certain temperature (below the melting point of the material). And then, a bed of powder is partially targeted (sintered) by a laser beam in order to fuse the powder materials into a predefined 2D shape/contour (based on the 3D model) on the surface of the powder bed. The top surface of the powder bed is refilled with a fresh layer of powder (from the refilling powder chamber) covering the sintered cross-section [22, 26]. This process is repeated until the desired 3D object is completed. Many types of materials including polymers, ceramics, metals and composites may be used as printing material in this 3D printing technology [25-27]. It is possible to easily print complicated shapes with SLS as this process does not need structural support since the powder bed acts as support for the printed item [28, 29]. Laser power, powder particle size, scan speed and scan spacing are the factors that define the quality of an SLS print [30].

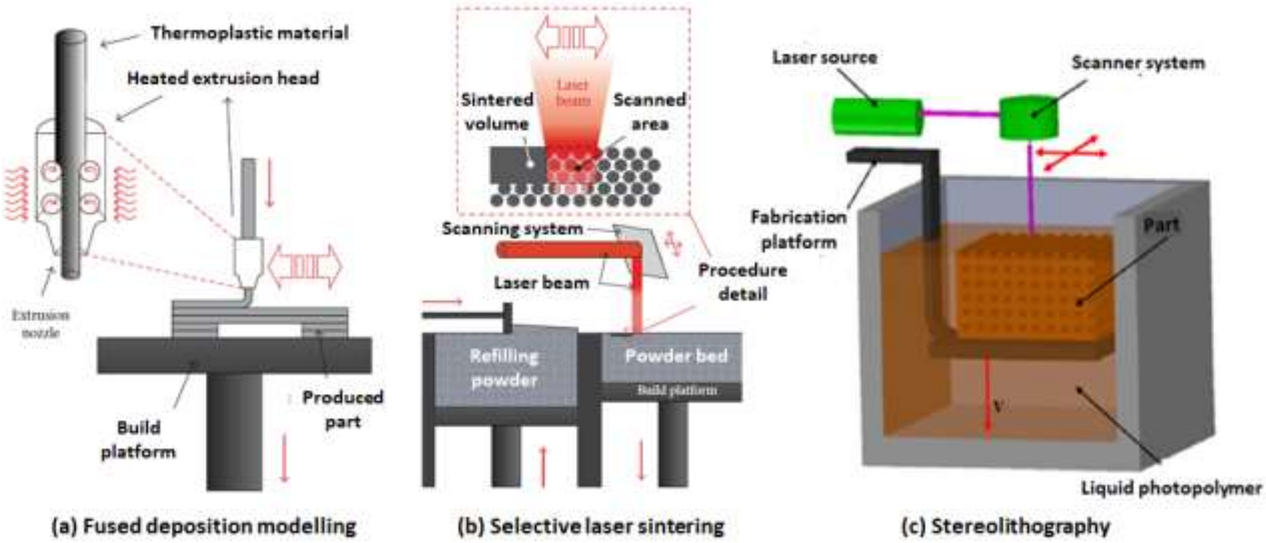

Figure 4. Schematic representation of the most common 3D printing techniques: (a) Fused deposition modelling (FDM) (adapted from [25]); (b) selective laser sintering (SLS) (adapted from [25]), and; (c) stereolitography (SLA) (adapted from [22]).

Stereolithography (SLA) is an additive manufacturing process wherein a part is created by selectively curing a (liquid) photosensitive thermoset polymer resin layer-by-layer using an ultraviolet (UV) laser beam, as shown in **Figure 4c**. This was the first AM technique developed [18]. The build platform is initially positioned in the vat with liquid photopolymer resin, at a distance of one layer height from the surface of the liquid resin. Then, the UV laser creates the next layer by selectively curing (polymerizing) the resin. The laser beam follows a predetermined path based on the cross-sectional area of the 3D model. After curing a layer, the build platform moves down (in other configurations, moves up) and the sweeper/wiper recoats the surface with a new layer of resin. This process is repeated until the part is complete. Postprocessing may be needed in order to achieve optimum thermo-mechanical properties. With this technique, high resolution could be achieved [18]. Similar to SLA, DLP uses photopolymers as 3D printing materials. The only difference is that DLP uses a different light source, e.g. an arc lamp with a liquid crystal display panel or micromirrors. This is then applied to the entire surface of the vat of thermoset photopolymer resin in a single projection, technically making it a faster process than SLA [18].

The 3D printing technologies presented here provides insights representing almost all 3D printing processes used for rapid prototyping. Specifically, representative 3D printing technologies using different printing materials (i.e. solid-based, powder-based and liquid-based) have been discussed. Other AM technologies may be found from recent publications [17-19]. A comprehensive summary covering most of the AM technologies and materials as well as the companies manufacturing them have been presented by Low et al. [13].

2.2. Mechanical properties of 3D-printed materials

For practical applications, several properties especially the mechanical properties of 3D-printed materials have to be considered. One major issue is the mechanical anisotropy which is different for various printing technologies, and is dependent on raster (layer) orientation. Due to poor interlayer bonding, weak tensile properties are observed when the 3D-printed samples are loaded along the build directions. Other factors to be considered which affect the mechanical properties of 3D-printed parts particularly FDM include layer thickness and air gap. Under compression loading, lower strength has been observed for parts having a transverse-build direction as compared with the sample having an axial build direction. The compressive strength of the part is less than 90% of the injection molded part. For SLA, build orientation and layer thickness affect the mechanical property of parts. Particularly, tensile strength increases with increasing layer thickness, while the impact strength and flexural strength decreases. For SLS, the mechanical properties depend on input energy, scan spacing, refresh rate, part orientation, feedstock uniformity, microstructure evolution, layer thickness, part bed temperature, hatch pattern, and laser beam speed. Mechanical anisotropy is also found with SLS-printed parts. Actually, there is varying anisotropy in 3D-printed parts with different printing technologies. **Table 1** presents the different factors affecting the mechanical properites of 3D printed materials fabricated by various techniques. A comprehensive discussion on the mechanical properties of 3D-printed parts is reported in our previous paper [18].

Table 1. Factors affecting the mechanical properties of various 3D printing technologies

3D printing technology	**Factors affecting the mechanical properties**
Fused Deposition Modelling (FDM)	Build direction, layer thickness, air gap
Stereolithography (SLA)	Build orientation and layer thickness
Selective Laser Sintering (SLS)	Input energy, scan spacing, refresh rate, part orientation, feedstock uniformity, microstructure evolution, layer thickness, part bed temperature, hatch pattern, and laser beamspeed
Digital Light Processing (DLP)	Build direction, pixelation
Three-Dimensional Printing (3DP)	Internal structure, binder content, sintering temperature, binder adsorption, mechanical locking, bonding between adjacent powders and adjacent layers
Polyjet	Printing orientation, post-processing, part spacing along the y-axis, aging
Laminated Object Manufacturing	Printing orientation

3. 3D-printed materials for membrane separation, desalination and water treatment

In recent years, AM (3D printing) has provided remarkable advancements in membrane module design, composite membrane fabrication, development of oil-water separation and wastewater treatment materials, etc. despite the limitations on cost, speed, printing resolution and material selection. Increasing number of research groups are utilizing 3D printing for designing complicated structures with ease of prototyping and tests for various water-related applications. **Table 2** lists various water-related applications as reported in literature using 3D printing to prepare all or parts of the main materials used for various water-related applications. From the table, it can be deduced that FDM, SLS, SLA and polyjet are the most commonly used methods to 3D-print their materials depending on the target applications. Discussions on each application are detailed in the following sub-sections.

Table 2. Comprehensive list of various materials prepared by 3D printing for water-related applications including details on the materials used, the 3D printing technique, the printed part and their corresponding applications (Abbreviations: SLS – selective laser sintering; FDM – fused deposition modeling; DLP – digital light processing; FFF – fused filament fabrication; SLA – stereolitography; RO – reverse osmosis; MD – membrane distillation; MF – microfiltration; NF – nanofiltration; UF –ultrafiltration; FO – forward osmosis).

Technology/application	3D-printed part	Material	3D printing technique	Refs
(a) Membrane separation				
Spacers				
RO, UF	Spacer	Polyamide 12 (PA 2202 (black) Thermoplastic)	SLS	[7]
MD	Spacer	Polyamide 12 (PA 2202 (black) Thermoplastic)	SLS	[8, 31, 32]
Filtration	Spacer	Polypropylene (PP)	SLS	[33]
Filtration	Spacer	Polyamide 12 based white powder PA2200	FDM SLS Polyjet	[34]
NF, RO	Spacer	Urethane acrylate polymer	Polyjet	[35]
MF	Vibrating spacer	Solid polyamide	SLS + Simulation by COMSOL	[36]
UF	Spacer	Liquid resin (Acrylate monomer)	DLP	[37]
FO	Spacer	Polypropylene, Polylactic acid (PLA), Acrylonitrile butadiene styrene (ABS)	Polyjet, FDM	[9]
Filtration	Spacer	-	SLS	[6]
Filtration	Spacer	-	SLS	[38]
RO, UF	Spacer	Acrylonitrile butadiene styrene (ABS)	FDM	[39]
UF	Spacer	-	SLA	[40]
UF	Spacer	-	Polyjet	[41, 42]
UF	Spacer	acrylate monomer	DLP	[43]
Membranes				
RO, NF	Thin film composite membrane	Fluorinated diamine incorporated into an m-phenylenediamine-based polyamide	Inkjet printing + interfacial polymerization	[44]
UF	Composite Membrane	ABS-like substrate	Multijet printing	[12, 45]
Advanced water treatment	Biocatalytic membrane	Polyvinyl alcohol (PVA) + yeast cells	Inkjet printing	[46]
-	Membrane	PLA, Polybenzimidazole (PBI), PVA	Solvent cast printing (SCP), FFF	[47]
Filtration	Ceramic membrane	Kankara clay powder + maltodextrin powder	Inkjet	[11]
RO	Thin film composite membrane	metaphenylene diamine (MPD) and trimesoyl chloride (TMC)	Electrospraying (for the active layer)	[48]
Oil-water separation	Membrane	Polysulfone	SLS	[49]
Oil-water separation	Membrane	Polyamide 12 (PA 2200)	SLS	[50]

Anion exchange	Anion exchange membrane	Quaternized poly(DUDA-co-PEGDA-co-VBC)	-	[51]
Gas-liquid contactors	Moulded membrane	Polydimethylsiloxane (PDMS)	DLP	[10]
(b) Wastewater treatment				
Degradation of pharmaceuticals	Capsules filled with ferrate	PVA	Lab-made printer	[52]
Biofilm reactor	Fullerene-inspired bio-carrier media	Nylon	SLS	[53]
Moving bed biofilm reactor (MBBR)	Biofilter media carrier	Liquid acrylate-based monomer resin	Polyjet	[54]
(c) Solar steam generation				
Desalination	Solar evaporator with concave structure	Nanofibrillated cellulose (NFC) with graphene oxide (GO) and carbon nanotubes (CNT)	FDM	[55]
Desalination	Jelly-fish like solar evaporator	Porous carbon black/graphene oxide + aligned GO pillars + expanded polystyrene	Vertical 3D printing	[56]
	Hybrid aerogel membrane	2D carbon nitride	Direct writing	[57]
(d) Adsorption/dye degradation				
MB removal	MOF composite	ABS coated with Cu-BTC (BTC = benzene tricarboxylic acid) metal-organic frameworks	FDM	[58]
Rhodamine B degradation	Zeolitic Imidazole Framework (ZIF-67)/ polymer mixed matrix on 3D printed device	-	SLA	[59]
(e) Oil-water separation				
Oil-water separation	Egg-beater superhydrophobic structure	E-glass with carbon nanotubes	Immersed surface accumulation based 3D (ISA-3D) printing	[60]
Oil-water separation	Oil skimmer mesh	-	SLA	[61]
Oil-water separation	Ceramic mesh	Alumina	DLP	[62]
Oil-water separation	Porous membrane	PDMS	DLP	[63]

3.1. Channel feed spacers

For many membrane separation applications especially using spiral wound membranes (SWM), feed channel spacers serve a very significant role in ensuring continuous flow and recirculation as well as fluid mixing [64]. Feed spacers come in various designs with the goal of enhancing turbulence, maintaining constant space (mechanical support) for fluid to pass through, reducing fouling formation, and preventing damage of the active layer of the membrane [3]. **Figure 5** (top image) shows the schematic diagram of how the spacer is placed in the module and the comparative dimensional requirements for various parts of the membrane module - from the membranes, spacers, and module sizes. As the spacer needs to be rolled up, it needs a balance of stiffness and flexibility, as well as good chemical resistance, thus commercial spacers are usually made of polypropylene (PP) [33]. Good spacer design is important as dead zones create situations for particle deposition leading to fouling that reduces mass transfer rate. Different spacer designs with various characteristics have been tested to limit dead zones and to determine its effect on mass transfer, pressure drop, and fouling [64, 65]. However, the complex spacer design and geometry can pose manufacturing challenges using conventional techniques such as heat extrusion, moulding or vacuum foaming. Hence, the potential of 3D printing in fabricating complex-design feed spacer is considered due to its ability to fabricate any simple or complicated geometries.

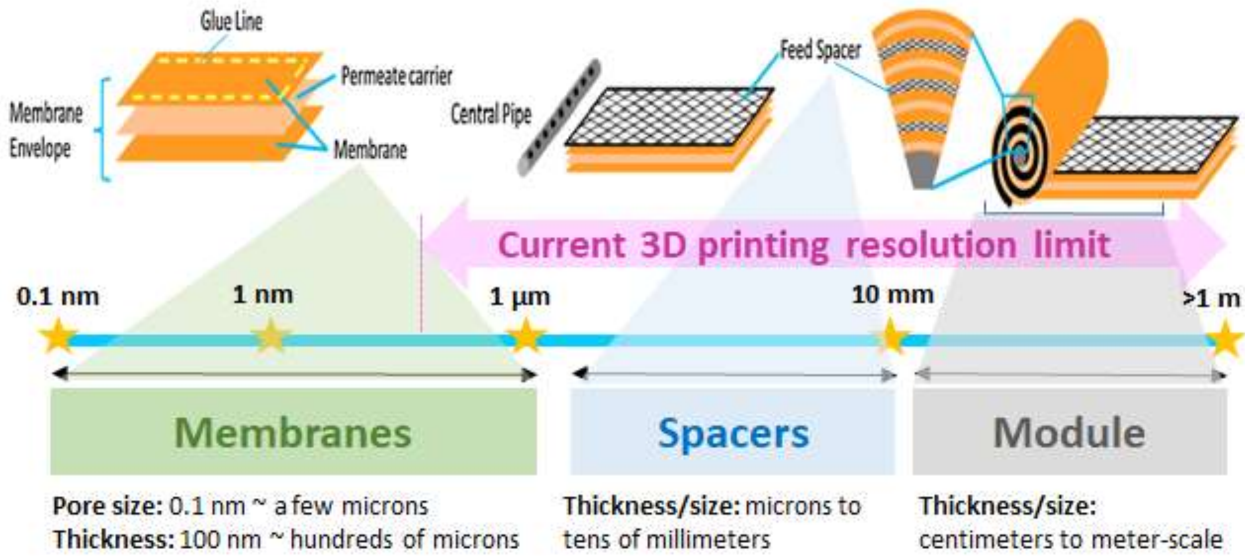

Figure 5. Top image shows the schematic of the spiral wound membrane (SWM) module components including the feed spacer (modified from [33]). The bottom image illustrates the comparative dimensions of the different parts of a membrane unit, and the current resolution limitations of 3D printing (modified from [3]).

Researchers have reported various spacer designs and geometries using 3D printing since the first report in 2014 [3, 66]. Among the spacer designs include triply periodic minimal surfaces, multi-layered spacer structures, herringbone and helices, twisted tapes, ladders, etc. [3]. These spacers were fabricated using different types of 3D printing techniques and printing materials. **Table 3** and **Figure 6** show a summary of the various 3D-printed feed spacers reported to date. Most of the spacers were mainly printed by SLS, FDM, DLP, and polyjet methods. A series of research work by Arafat et al. [7, 8, 32] investigated various 3D-printed spacer designs for membrane performance enhancement and fouling control (see **Fig. 6a**). For example, they [7] proposed a triply periodic minimal surface (TPMS) spacer design to enhance flux performance and fouling resistance of RO and UF processes. Their TPMS design was based on its success for use in heat exchanger units. Desalination tests showed flux enhancements of 15.5% (for brackish water RO) and 38% (for UF) when compared with those using commercial polypropylene feed spacer. Biofouling formation was reduced using TPMS while minimizing pressure drop across the membrane. The same TPMS spacer design was further tested for MD scaling control [8] and organic fouling [32] in their subsequent studies. Using calcium sulfate (at 1900 mg/L) as model foulant [8], the TPMS (particularly tCLP) achieved 50% higher flux and less membrane scaling compared to a commercial spacer. However, pressure drop was found to be higher. Combining the tCLP and gyroid design into one spacer maintained high flux, low membrane scaling, but at a lower pressure. Interestingly, it was noted that the micro-surface roughness of the TPMS enhanced scale formation on the spacer itself. But the same TPMS design also resulted to lower organic fouling formation [32]. In order to maintain high recovery rate, fouling pre-treatment and cleaning-in-place for both membrane and spacers are necessary.

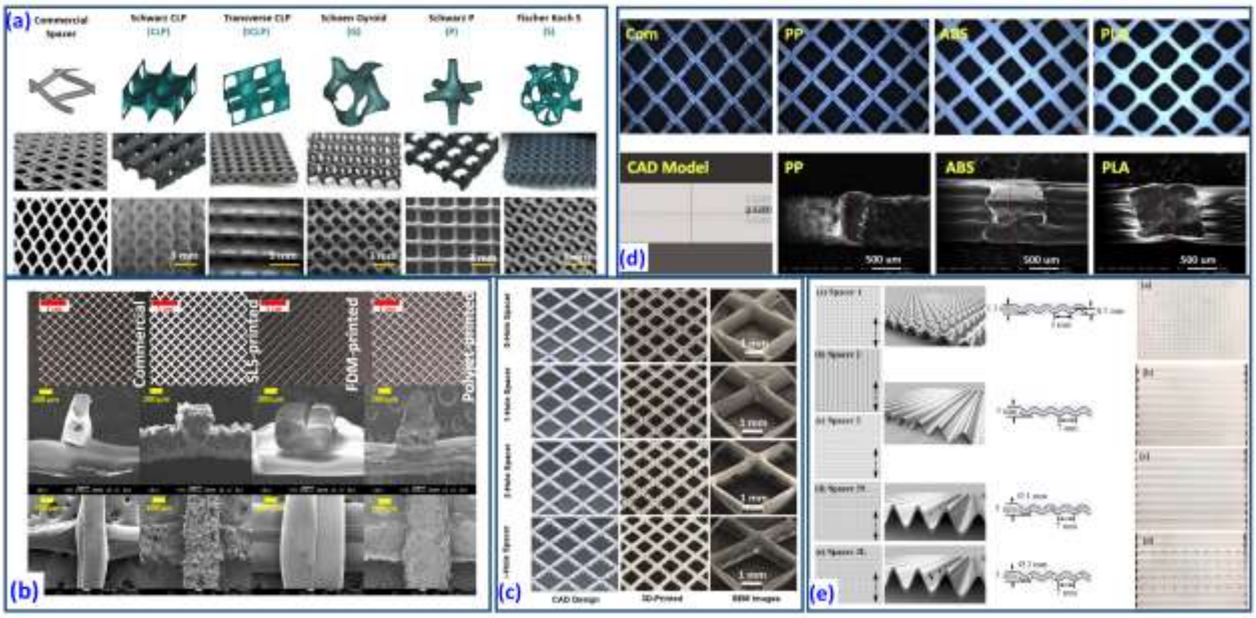

Figure 6. Some example designs of 3D-printed spacers reported in literature: (a) Various designs of commercial and 3D-printed triply periodic minimal surfaces (TPMS) spacers: representative volume element (top row), photographic images (middle row), SEM images (bottom row) [7]; (b) photographic and SEM images of different 3D-printed spacers printed by SLS, FDM and polyjet in comparison with the commercial net spacer [34]; (c) CAD models, and the photographic and SEM images of the 3D-printed spacers with 0-hole, 1-hole, 2-hole and 3-hole spacer [37]; (d) Stereo fluorescence images of commercial and 3D-printed spacers made of PP, ABS and PLA with various designs, and the corresponding SEM images of the 3D-printed spacers and a CAD model for thickness comparison; (e) Different designs of polyamide 3D-printed spacers with repeating hill-like structures and wave-like protrusions with and without perforations (vibration capability).

Tan et al. [33] prepared a net-type feed spacer made of polypropylene (PP) by the SLS method. They investigated the optimum building temperature and process parameters in 3D printing the PP spacer. The accuracy of printing and mechanical properties of the printed part were evaluated. Results indicated that the energy density (laser power, scanning speed and scanning distance) used was proportional to the Young's modulus, and ultimate tensile strength. Meaning, the higher energy density, the higher the Young's modulus and ultimate tensile strength of the printed part. However, the accuracy of the dimensions was found to have a correlation with the Young's modulus of the PP material. In their subsequent study, [34] three 3D-printing methods were compared, namely, SLS, polyjet and FDM on their geometry and surface finish. Their membrane performance and fouling properties were also considered (see **Fig. 6b**). Regardless of the printing method it was found that the 3D-printed spacers maintained superior mass transfer performance at fixed power consumption and critical flux when compared with a commercial spacer. In terms of printing accurateness, their tests showed a preference of: polyjet>SLS>FDM. Further consideration can be made on the; (a) geometric printability, (b) model to part accuracy, and (c) surface finish when fabricating spacers.

Kerdi et al. [37] tested three symmetric perforated spacer designs (1-hole, 2-hole and 3-hole) fabricated by DLP 3D printing on their hydrodynamic performance and filtration efficiency in ultrafiltration test. Direct numerical simulation was carried out to further enhance the understanding of their performance and mechanism. They hypothesized that the perforations in the new design would increase the shear stress at the membrane surface thereby reducing fouling, and at the same time reduce the net pressure in the module. Under ultrafiltration tests, the perforated 3D printed membranes compared to non-perforated ones showed better filtration performance due to the presence of micro-jets as induced by the perforations through elimination of dead zones. The 1-hole spacer obtained the best performance among all designs, showing 75% (under constant pressure) and 23% (under constant feed flow) improvements in permeate flux, and had the cleanest membrane surface (less fouling). The 3-hole spacer showed high reduction in pressure drop (54%) but did not translate to increased permeation flux. Also, increasing the number of perforations resulted to more fouling due to reduction in unsteadiness of water flow. Overall, the three different perforated designs resulted in thinner fouling formation compared to 0-hole spacer. The optimum spacer design was concluded to be the 1-hole spacer based on the conditions of this study. In a similar manner, Ali et al. [43] utilized DLP to print their spacer with column designs. With their design, they aimed to increase the clearance between the filament and the membrane, while maintaining the same flow channel thickness. The column type nodes were added to act as vortex shading structures. Numerical analysis showed less pressure drop using their 3D printed spacer, including lesser dead zones as also proven by their experimental results. When compared with standard commercial spacer, the 3D-printed spacer with column design obtained two orders of magnitude lower specific energy consumption than the standard spacer. Using polyjet and FDM 3D printing, Yanar et al. [9] investigated the mechanical properties, flux and fouling performance under FO operation of three diamond-shaped spacer made from ABS, polylactic acid (PLA) and PP (see **Fig. 6d**). The reference spacer was a commercial PP spacer with diamond shape design. The study found that the material and the kind of 3D printing technique used have a corresponding effect on the spacer properties and performance. PP and PLA were found to have best FO performance, particularly in terms of reverse solute flux and fouling resistance. Fouling resistance was found much better when using PLA (10% less) when compared with the commercial PP spacer. In another study, vibrating 3D-printed spacers with unique designs (see **Fig. 6e**) were prepared by Tan et al. [36] using SLS method together with COMSOL simulation. The aim was to determine the effect of spacer configuration and vibration configuration on fouling control in a submerged microfiltration system environment. It was concluded that the spacer design and configuration affected the extent of fouling control performance, with wavy design outperforming the hill-structure design. Also, smaller perforations performed better compared to larger perforations.

Based on literature, feed spacer materials have been one of the most researched materials for 3D printing application in recent years especially for desalination and water treatment. This is primarily due to the suitable printable resolution in current 3D printers, wherein complex designs can easily be fabricated. Most results on 3D-printed spacers indicate better performance in terms of flux performance, control of fouling, and even improving hydrodynamic flow compared to commercially available spacers. However, the surface finish needs further improvement for many 3D printed spacers. In addition, availability of more materials for 3D printing with good mechanical and surface properties in compartmentalized modules is attractive.

Table 3. Various 3D-printed feed spacers reported in literature with details on the design/geometry, materials used, 3D printing technique and their intended applications (Abbreviations: RO – reverse osmosis; MD – membrane distillation; NF – nanofiltration; UF –ultrafiltration; FO – forward osmosis; DCDM – direct contact MD).

Spacer design and material	3D printing technique	Application	Remarks	Ref
Triply periodic minimal surfaces (TPMS), tCLP and Gyroid	Selective laser sintering (SLS)	MD	- Scaling (calcium sulfate) control in DCMD. - 50% higher flux for tCLP compared to commercial spacer. - Lesser scaling for membranes using TPMS spacer.	[8]
Triply periodic minimal surfaces (TPMS)	Selective laser sintering (SLS)	RO, UF	- Compared with a commercial membrane, TPMS spacers showed flux enhancements of	[7]

			15% for brackish water RO and 38% for UF. - Biofouling was found to be lesser using TPMS.	
Triply periodic minimal surfaces (TPMS) – gyroid and tCLP	Selective laser sintering (SLS)	DCMD	- 50-65% flux enhancement when using TPMS compared to commercial membrane. - Gyroid design: better organic fouling control - 99% salt rejection and better permeate quality.	[32]
Polypropylene net structures	Selective laser sintering (SLS)	Spiral wound membrane modules for water industry	- Investigated the printability of PP polymer for net-type spacer structures. - Found that SLS can successfully print PP into spacers. - Higher printing energy density used resulted to better mechanical properties. - Found there is correlation of accuracy of dimensions and the resulting Young's modulus.	[33]
Polyamide 12, ABSplus™, Acrylic based monomer VeroClear net spacers	FDM, SLS and Polyjet	Spiral wound membrane modules	- Compared three 3D printing techniques: FDM, SLS and polyjet for their printing ability - All spacers by the three techniques showed better mass transfer at fixed power consumption and critical flux	[34]
Urethane acrylate polyer - Modified filament angle, modified mesh size, and combination of both designs	Polyjet	RO and NF	- Results: 3D printing can copy the current spacers used in practice with similar results in hydrodynamics, pressure drop and biofouling. - Modifying the design slightly (filament angle, mesh size, or both) from commercial spacer using 3D printing can result in lesser pressure drop and biofouling. - FDM and SLA: found not suitable printing techniques for the present spacers	[35]
Symmetric perforated spacers, Acrylate Monomer	Digital light processing (DLP)	UF	- Hydrodynamic changes, filtration tests and fouling. - Perforated spacers lowered the net pressure drop (with 3-hole having lowest pressure drop). - 1-hole spacer was the most efficient in terms of permeate flux enhancement and least fouling.	[37]

Acrylonitrile butadiene styrene (ABS), polypropylene (PP), and natural polylactic acid (PLA) – diamond-shape feed spacer	PolyJet, FDM	FO	- Comparison of performance of three materials for 3D printing of diamond-shaped spacers: ABS, PP and PLA. - Similar results for water flux, but the 3D printed spacers gave better reverse solute flux and fouling resistance compared with commercial spacer. - PP and PLA had best performance with PLA as having 10% less fouling.	[9]
Acrylate monomer column type design	Digital light processing (DLP)	UF	- Column spacer reduced the pressure drop by three times and doubled the specific water flux. - Less bioaccumulation on the column type spacer - Specific energy consumption - two folds lower than standard spacer	[43]

3.2. Membranes for filtration and water treatment

Membrane technology is rapidly advancing and has replaced many conventional water treatment processes due to its high efficiency and cost-effectiveness [67, 68]. Majority of the membranes used are made of polymers but ceramic membranes are also utilized. Conventional polymeric membrane fabrication techniques include phase inversion [69], hollow fiber spinning [70], stretching, and extrusion. Increasing number of studies have also focused on the electrospinning technique for various desalination and water treatment applications [71-73]. The capability of 3D printing to precisely fabricate hierarchical structures and scale is promising for membrane fabrication. However, due to resolution and materials limit, 3D printing is not yet widely investigated for direct polymeric membrane development [3]. Most available 3D printers are not yet able to efficiently print below submicron resolution, where membrane pores are usually in that range. In addition, some membrane applications require specific types of material characteristics and wettability (hydrophilic or hydrophobic), rendering it a challenge as current 3D printers are limited to their applicable/printable materials. Still, a few research groups have started to demonstrate the potential of 3D printing for membrane-related fabrication, usually in the form of composite membrane, i.e., with 3D-printing used for the substrate, and other techniques to fabricate the active layer.

Shimerry et al. [12] investigated the performance and anti-fouling behavior of a composite membrane composed of 3D-printed ABS-like support layer (with flat and wavy surface structures) by multijet printing and a thin polyethersulfone (PES) selective layer. The PES layer was casted on top of the support layer via phase inversion. **Figure 7** shows the schematic of the fabrication process and the photographic and SEM images of their composite membrane. The authors carried out ultrafiltration tests to investigate the performance of the fabricated membrane based on their permeation, oil rejection and anti-fouling behaviour. Fouling, which is the deposition of unwanted materials on/in the membranes, is a major challenge for all membrane separation processes as it reduces the efficiency, performance and life of a membrane [74]. For fouling test, oil-in-water emulsion was used as model foulant to check the fouling resistance of the 3D-printed composite membrane. Under 1 bar transmembrane pressure, results indicated better permeability for the wavy membrane (30% higher) compared to the flat membrane, while maintaining high oil rejection (96%). The wavy membrane also has less fouling and proved easier to clean even with water only than the flat membrane. The authors claimed composite membranes have comparable results with PES mixed matrix membranes reported in literature but was much better than pure PES membranes. Their subsequent report [45] indicated better bovine serum albumin (BSA) fouling resistance of their composite membrane with wavy support, even retaining >80% initial permeance after 10 test cycles with water as the only cleaning agent. Though initial results are promising, the report lacked information on the potential delamination of the selective layer for long-term operation, and the challenge of upscaling or modulation as the 3D-printed support layer may be too stiff and not easy to bend for module preparation.

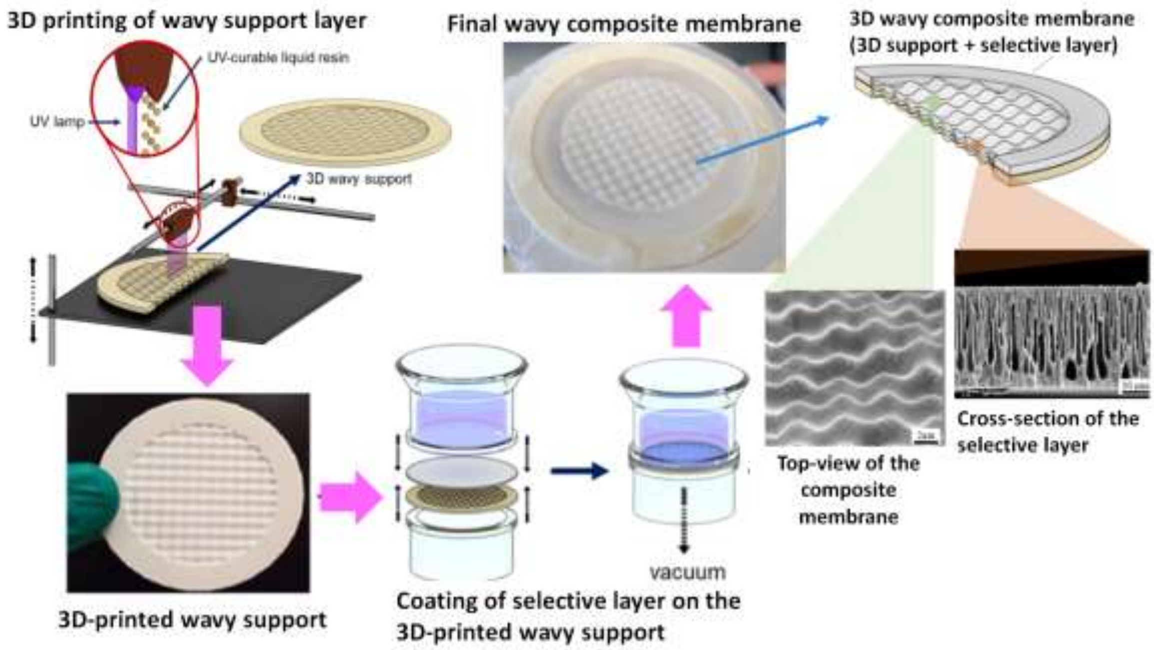

Figure 7. Schematic of the composite membrane: support layer was 3D-printed with wavy design while the selective layer on top was first casted by non-solvent induced phase separation (NIPS), then the casted membrane is attached on the 3D-printed support by vacuum filtration (figure was modified from [12] and [45]).

Compared with other common 3D printing techniques, Chowdhury et al. [48] demonstrated the potential of electrospraying as a variant of 3D printing to fabricate a very thin polyamide selective layer of a thin film composite (TFC) RO membrane. TFC membranes are composed of a very thin and dense polyamide selective layer, a middle support layer, and a thick backing layer for mechanical support. The most important part of the membrane is the ultrathin selective layer, as this is where the separation process takes place. Though conventional TFC membranes are considered as state-of-the-art membranes for desalination with high permselectivity, the synthesis of the selective layer is not easy to control. Most especially, the thickness and roughness of the selective layer are important to affect the flux, selectivity and fouling tendency of the membrane. To precisely control the selective layer thickness, Chowdhury et al. [48] directly deposited monomers (m-phenylene diamine (MPD) and trimesoyl chloride (TMC)) by electrospraying onto a UF substrate to form the polyamide layer. **Figure 8** shows the schematic of the electrospraying system, the fabrication process and the example images of the fabricated selective thin polyamide layer and its corresponding scanning electron microscopy (SEM) image. Since the electrospraying produced droplets on the substrate surface in an additive way, its thickness could be controlled more precisely as well as the resulting roughness. With this approach, they were able to control the thickness up to 15 nm with resolution of around 4 nm, and roughness resolution of up to 2 nm. The permselectivity and flux performance were also found to be comparable with a commercial TFC membrane. It is noted though that this process is not in the truest sense of 3D printing process as there was no 3D CAD models made, and no slicing done on the model for printing.

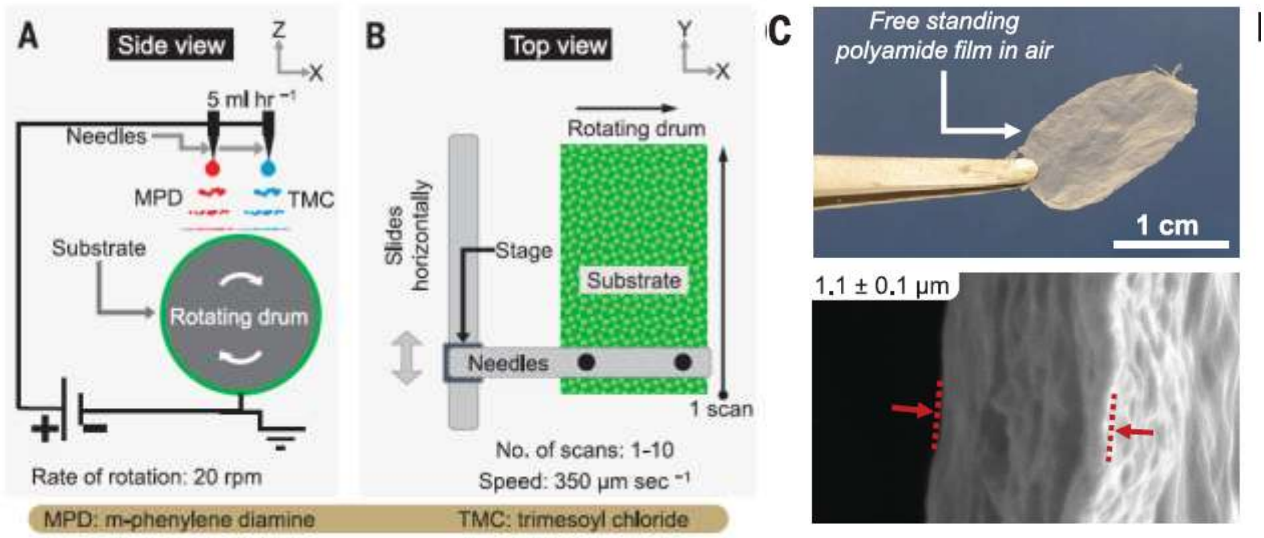

Figure 8. (a, b) Schematic of electrospraying process for printing polyamide films; (c) photographic image of a free-standing electrosprayed polyamide thin film and its corresponding SEM cross-sectional image (adapted from [48]).

Yuan et al. [50] prepared a ZIF-L decorated 3D-printed polyamide (PA) membrane substrate (SLS-printed) with superhydrophobic and underwater superoleophobic surface. Two steps were involved in the preparation of the composite membrane. The first was the synthesis of two kinds of uniquely-shaped ZIF-L particles and the second step was the deposition of the ZIF-Ls on the 3D-printed PA substrate. Upon the application of the 3D-printed composite membrane in oil-water separation, it achieved a separation efficiency of over 99% and an oil flux of 24,000 LMH.

Among various 3D printing techniques, the liquid-based DLP was used by Wessling's group to print directly a polydimethylsiloxane (PDMS) membrane for gas-liquid contact based on Schwarz-P triple periodic minimal surface (TPMS) design. This study was considered the first report of 3D printed membrane. PDMS has a high permeability for various gases. However, it has shown a 15% lower permeability due to its thickness of 840 µm and higher crosslinking density in the printed membrane [13, 75]. The same group has reported an indirect printing of PDMS with complicated geometries using a sacrificial mold that serves as a template for membrane design and fabrication. The membrane has shown an improvement in terms of mass transfer, but still thicker than conventional membranes.

Mecham et al. proposed the production of thin membranes through the continuous liquid interface production (CLIP) method based on a DLP system for resin formulations. This method has capability of printing objects continuously instead of layer-by-layer thereby enhancing the printing speed. The group reported on the potential of this method in production of thin supported membrane structures for water and gas separation by using a wide variety of polymers. They also addressed the potential of exploring the influence of process parameters on the permeation and separation characteristics [76]. Recently, a study using an enhanced CLIP method was reported by Lin's group. The method utilizes a track-etched membrane (TEM) which serves as the oxygen-permeable window during the process. Due to high oxygen permeability of TEM, the printing speed of the manufacturing process is measured up to 800 mm per hour using pure oxygen and 470 mm per hour even when using air [77]. Hwa et al. [11] investigated the performance of a 3D-printed Kanakra clay powder ceramic membrane for water filtration. The fabricated samples could be sintered to 1300^{o}C to produce porous membranes. They determined the effect of clay powder size on the membrane efficiency where their membrane was found adequate for membrane filtration at an inexpensive price using clay, with acceptable efficiency and functionality.

It is worth noting the increasing research activities to fabricate separation membranes by 3D printing with the resolution limit and the applicable material being two hindrances that negate its full exploration. As illustrated in **Fig. 5**, the resolution limit of most commercial 3D printers are not high enough to accurately print the pore sizes and tolerances needed. Though some 3D printers such as two photon polymerization (TPP) process can print sub-micron resolution, they are still limited to their printing consistency and tolerance/surface finish, i.e., the prepared model cannot be printed precisely as designed. Also many membranes require far smaller pore sizes such as those for ultrafiltration, nanofiltration and reverse osmosis (non-porous). Due to this limitation, perhaps the approach should be to explore more of the composite membrane designs, rather than to directly print the entire membrane. Another is to ensure good compatibility of the active layer and the support layer materials, preventing any delamination. Until such time that higher resolution capability (i.e., up to nanometer level) can be produced by newer and better 3D printers, the direct printing of membranes will remain a challenge. The limitation on applicable printing materials is also negating the direct use of 3D printers for membrane fabrication.

3.3. Photocatalytic material

Heterogeneous photocatalysis works by oxidizing the polluting compounds through the reaction of a semiconductor material that is activated upon exposure of a light source at specific wavelengths [78]. The use of photocatalytic materials such as titanium dioxide (TiO_2) can dramatically increase the rate of water and wastewater treatment. When exposed to light, the catalyst absorbs photon with a larger bandgap, then the formed electron-hole pair allows the catalyst to react with water and dissolved oxygen to generate hydroxyl radicals (OH) and oxide radicals (O_2^-) [79]. In many cases, the material needs to be immobilized on a substrate in order to prevent secondary pollution from the catalysts themselves, and to enable re-use of such photocatalysts. One major issue in conventional photocatalyst substrate is the smaller surface area. Other newer substrates now offer enhanced surface area for photocatalyst immobilization but could pose challenges in synthesis or in making catalytic materials strongly adhered on the substrate. This can potentially be addressed by proper design and fabrication of substrate materials via 3D printing. The main advantage of 3D printing is its capability to finely tune the structure of the target photocatalytic material.

Due to very high porosity, specific surface area, and self-supported structures of 3D printed photocatalytic materials, they can be exposed to sunlight enabling efficient solar spectrum absorption. Andrey et al. used stereolithography-based 3D printing to pattern the synthesized titanium-rich photoresist using a layer-by-layer approach with 25 µm layer thickness [80]. Structures with different geometries were printed, with UV exposure of the first layer for 14.0 s, four consequent layers for 9.0 s, and all remaining layers for 3.5 s. The process involved pyrolyzing at 1000 °C under an inert Ar atmosphere, a cubic and octet titania lattice structures with 0.65-1.50 mm unit cells, 115-170 µm beam diameters, and 11-31 relative densities. The SEM results showed beams and unit cells with uniform sizes and a visible layer-to-layer transition patterns. The surface of the structure is uniformly covered by porous nanocrystalline and crystals size ranging from 20 to 150 nm. In comparison to titanium foam, the 3D printed part exhibited more strength. Furthermore, the as-designed photocatalytic structure enabled solar water disinfection via the porous structure without using an additional filter. Sangiorgi et. al reported the 3D FDM printing for the preparation of TiO_2 nanoparticles utilizing PLA as environmental friendly biopolymers. The structured materials showed 100 % methylene blue (MB) degradation after exposure to light for 24 hours [81]. Vidales et al. reported the AM of titania via depositing TiO_2 in low-density-polyethylene (LDPE) as floated photocatalyst using FDL [82]. The materials were fabricated by two different methods: (a) through mixing LDPE and TiO_2 in a hot-cylinder-mixer, and (b) by dispersing TiO_2 and LDPE using o-xylene or an anionic surfactant as a dispersing agent, in order to enhance the dispersion of TiO_2 in the filament before the extrusion process. They investigated the effect of the surface deposition of the printed materials through printing precursors onto TiO_2 mesh which further improves the catalyst performance toward MB degradation, compared to the conventional plate.

In photocatalysis, the photocatalytic material has to be exposed to the light at specific wavelength in order to maximize its photocatalytic performance. Thus, it is important that this aspect should be considered in the design of substrate material. 3D printing enables production even for very complicated geometries, thus potentially open-cell architecture designs or even those involving fractal designs can be easily fabricated. This open-cell design can allow the light to propagate along the bulk of the photocatalytic material, thus enhancing its overall photocatalytic efficiency. The main challenge with complicated structure is on how to uniformly immobilize the inorganic photocatalytic material on the entire material surface. This can be addressed by preparing a feedstock polymer that has been incorporated with photocatalysts such as titania and then subjecting to pyrolysis to obtain the titania-decorated open-cell structure along the whole surface [83]. Another approach is by impregnation process of photocatalytic material onto a 3D-printed supporting structure [78]. Research by de Rancourt de Mimerand et al. [84] reported the preparation of a very complicated fractal-based 3D-printed (by FDM) structure that was plasma-activated to produce a hybrid photocatalyst fractal structures in the form of fractal pyramids (fracmids). The lamellar fracmids are ideal for photocatalysis as the structure is oriented to capture light efficiently, as proven by the positive outcome of their photocatalytic test results.

Though 3D printing offers exciting possibilities as an approach to fabricate photocatalytic materials with various designs, however, it does not come without any challenges. For 3D printing, polymers are most commonly used but they suffer from relatively low surface areas, varying thermal stability, and poor surface properties, making them not suitable for direct use in photocatalysis. Thus, in many cases, 3D-printed polymers are used to prepare the substrate for which inorganic photocatalytic nanoparticles are immobilized. For example, not all 3D printing methods and materials are suitable for catalytic applications. FDM mostly uses thermoplastic polymers such as ABS that have low glass transition temperature and low surface area [85], which make them unsuitable for photocatalytic applications as their properties may be affected by the application of heat and light. Increasing the activities of the material may help by incorporating inorganic particles in the polymer filament, but this can also suffer from potential polymer encapsulation of these nanoparticles, which can decrease their performance. To ensure exposure of highly active particles, one approach is to load them directly on the 3D printed material surface, however, delamination becomes an issue. Therefore, ensuring that the active material and the surface have strong interaction is a requisite. SLA printing also has a drawback in that it can only process photosensitive materials, which obviously is problematic for use in photocatalysis.

3.4. Capsules/bio-carriers for wastewater treatment

Wastewater streams are significant sources of microorganisms, pharmaceuticals, and various compounds that are difficult to be removed by conventional wastewater treatment systems. Post-treatment processes are usually needed to further treat the wastewater effluent. One of the effective ways to breaking down these compounds is through chemical oxidation. Chemical oxidation using ferrate(VI) has shown good efficiency in oxidizing organic and inorganic compounds [86]. However, ferrate(VI) is relatively expensive to produce and is highly unstable in humid environment. By simple encapsulation, ferrate(VI) can be made more stable and its release can be controlled, making it resilient and cost-effective. The capsulation and controlled-release strategy has been reported to be efficient in removing dissolved contaminants in water [87]. With this premise, Czolderova et al. [52] utilized 3D printing to prepare polyvinyl alcohol (PVA) capsules to encapsulate ferrate(VI) (**Fig. 9b**) and were compared with conventionally-made commercial capsules (**Fig. 9a**). Their results indicated long-term storage potential (more than one month without loss of efficiency) of their 3D-printed capsulated ferrate. The degradation efficiency however gave mixed results, achieving more than 80% to most of the micropollutants, but only achieved partial oxidation to others using real wastewater samples. The encapsulation approach using 3D printing in this study could potentially be used to store or apply ferrate in times of emergency. One limitation of the present approach is the multi-step process involving 3D printing of capsule and then loading of ferrate into the capsule. A potential strategy in the future may be a one-step approach of directly printing the capsule with ferrate, or in the form of an open or close construct (such as tablet type) with highly detailed structure to enable tuning of chemical release profiles. This can be made possible by multi-material printers such as those parts printed using polyjet technology.

Moving bed biofilm reactors (MBBRs) are widely used worldwide for wastewater treatment due to their simplicity and potential efficiency, allowing attached and suspended growth systems [88]. A lightweight with high-surface area-to-volume ratio carrier media is highly suitable for MBBR. The performance of the bio-carrier media highly depends on the formation of biofilms on its surface with good stability. The biofilm formation is affected by the operating conditions (hydrodynamic, nutrients and oxygen) and the bio-carrier design (i.e., physicochemical properties such as kind of material, surface properties and texture, pore spacing, and geometry) providing the growth environment, which affect the overall performance of MBBR. Having a good bio-carrier design would ensure that bacteria adheres to the maximum area possible, with good exposure to food and nutrients for survival and growth. Many carrier media with different designs are available commercially, and most of them are made with simple structures for ease of manufacture using conventional processes. Improvements in MBBR performance could potentially be achieved if more complex carrier media structures can be made to increase microbial stimulation and growth. 3D printing can design and produce complicated designs, thus it can potentially make the most ideal condition and design for bacterial growth. Elliot et al. [54] prepared a spherical gyroid-shaped carrier media via polyjet 3D printing (see **Fig. 9c**) and used in MBBR (schematic is given in **Fig. 9d**). They optimized their design by modelling and designing a 3D printed carrier with specific surface area (SSA) of up to more than 2300 m^2/m^3. Wastewater from fisheries was used for inoculation and the results indicated that their 3D printed gyroid media has comparable NH_3 removal when compared with the baseline K1 Kaldnes commercial media carrier. However, the exact mechanism of how the 3D printed media stimulates microbial assemblages and metabolism to affect reactor performance was not elucidated and is ought to be further investigated.

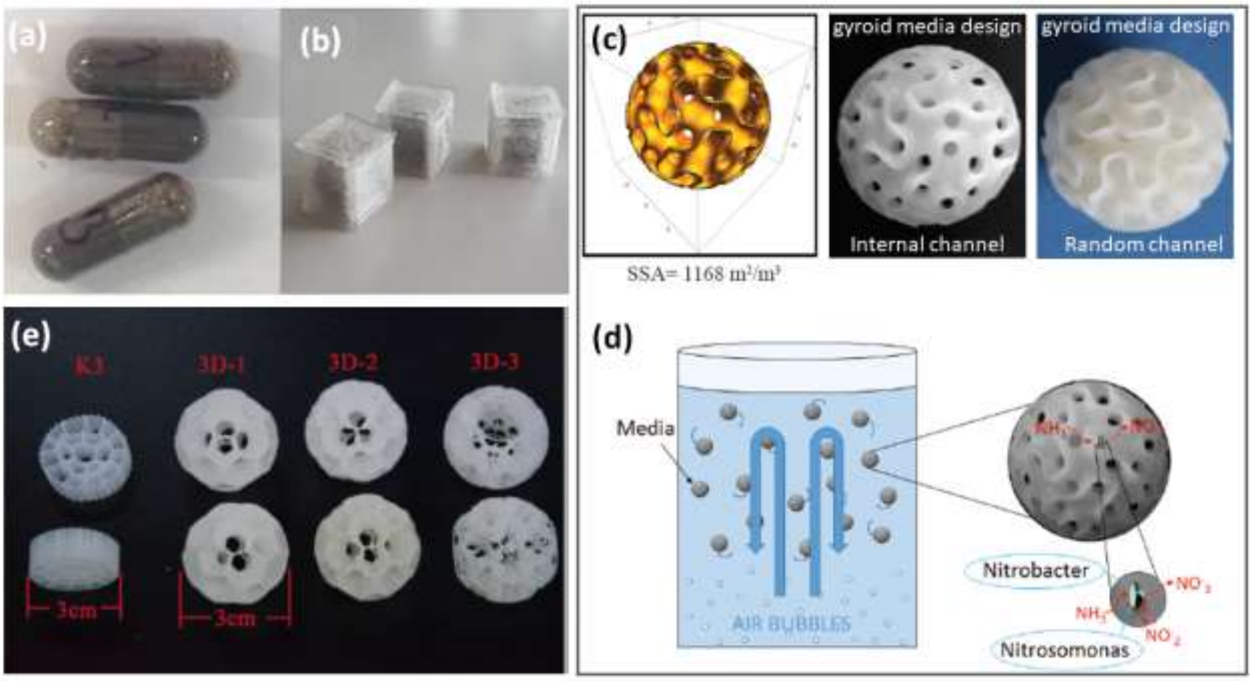

Figure 9. Chemical oxidation as post-treatment to break down compounds using encapsulated ferrates (a) commercial conventionally-prepared gelatin capsules, (b) 3D-printed polyvinyl alcohol (PVA) capsules [52]; (c) Different designs of fullerene-type 3D-printed nylon bio-carriers for wastewater treatment using sequencing biofilm batch reactor [53]; (d) various gyroid media designs fabricated by 3D printing (computer model, internal channel design, and random channel orientation design for moving bed bioreactor (MBBR) application. Schematic of the MBBR system is shown in (d) [54].

In another study, Dong et al. [53] designed and fabricated novel fullerene-design type bio-carriers using 3D printing. They intended their new bio-carriers made of nylon (with three designs – see **Fig. 9e**) to have specialized structures in order to improve its organic matter removal and overall performance in biofilm reactors. The physicochemical properties and biofilm growth performance of their bio-carrier was compared with a commercial K3 bio-carrier made of polyethylene (**Fig. 9e**). Results indicated greater surface roughness for their 3DP bio-carriers compared to K3 yet possess much better hydrophilicity. The better surface properties and the specialized hollow design resulted to higher microbial activity (8.73-27.60% higher than K3) and adhesion ability of their 3DP bio-carrier. Compared with fixed bio-carriers, the suspended bio-carriers are designed to move freely in the bioreactor under exposure to flowing water and air. This free motion improves the mass transfer process but can also lead to more collision of bio-carriers hereby causing friction and shearing between them, ultimately leading to slow biofilm formation. On the other hand, fixed bio-carriers can provide higher filling ratio in the bioreactor as they can be arranged homogeneously before operation. To address the limitations of both configurations, Tang et al. [89, 90] designed a semi-suspended spindle-shape bio-carrier media via 3D printing process in order to enjoy the potential high bio-carrier filling ratio in the bioreactor while also providing a restricted freedom of bio-carrier motion. The complexity of the spindle-shape bio-carrier design and structure makes it challenging to fabricate by conventional molding method, thus 3D printing comes into play. Results indicated good growth of diverse microbial community on the 3D-printed semi-suspended bio-carriers.

The sizes and resolutions needed to 3D-print capsules and bio-carriers for wastewater treatment are well within the capability of current 3D printers, thus making it as an attractive new option for preparing such materials. In addition, 3D printing can easily manufacture any complex design and structures, giving more leeway to test and prototype bio-carriers with increased surface area, and design that can stimulate new and diverse microbial community. This is in contrast with commercial bio-carriers where they are usually just based on simple patterned structures due to restrictions in conventional manufacturing processes such as polymer extrusion, injection molding, etc. Most of the recent studies on 3D printed bio-carriers have been mainly focused on developing new designs and shapes, and increasing the overall surface area. Future opportunities would be to investigate various surface texture, unique topology designs that provide robust features and dead zones that are essential for anaerobic growth of bacteria. 3D printing could potentially fabricate a novel carrier design involving heterogeneous flow environments (e.g., combined nitrification/de-nitrification process). There is no doubt that 3D printing will play a major role in the production of new generation bio-carriers/filter or capsules in the future.

3.5. Sorbents/substrates for oil-water separation

Oil spillage and pollution is one of the main environmental concerns during oil exploitation, extraction, and oil transportation. Oil-water separation technology has been gaining significant attention to address oil clean-up during times of oil spillage and oily discharges [91]. Among the many materials and methods used for oil clean-up, porous membrane structures as sorbents are showing great promise due to their high separation efficiency and recyclability. The porous material allows the oil to pass through the pores but inhibits the water at its surface. This is due to its special wettability (superhydrophobic-superhydrophilic) and high surface-area-to-volume ratio. However, conventional fabrication methods are time consuming and often involve complicated steps. 3D printing has been proposed as a facile way to prototype and fabricate near-ideal porous membrane structures with desirable properties for oil-water separation. Studies utilizing both polymeric and ceramic-based materials have been reported in recent years for oil-water separation.

The challenge of coating superhydrophobic structures at a micro/nano level on the surface of a substrate for oil-separation has driven Lv et al. [63] to use 3D printing technology. In their study, polydimethylsiloxane (PDMS) ink containing hydrophobic nanosilica was coated on a mesh structure by 3D printing. The presence of the nanosilica in the ink imparted good printability and provided mechanical strength on the coated material. Topographical structures to provide superhydrophobicity was controlled. A very high flux of 23,700 LMH was achieved and a water-oil separation efficiency of 99.6% at a pore size of 0.37 mm. Shin et al. [92] on the other hand got inspiration from nature (cactus plant) and prepared a bio-inspired PDMS sponge. A 3D printed mold served as template to fabricate the PDMS sponge. The sponge has a hollow, porous structure at the center that serves as the oil storage space. Results indicated the effect of surface pore size and line width on the absorption capacity, wherein the bigger pore size and decreasing line width lead to increasing capacity. The present bio-inspired PDMS sponge showed almost 4 orders of magnitude increase in absorption capacity compared to conventional PDMS sponge. Another study [93] prepared a bio-inspired (based on lotus leaf) 3D-printed (FDM technology) superhydrophobic poly(lactic acid) or PLA packings. A high oil-water separation of 95% and relatively high flux were achieved. Yuan et al. [49] used selective layer sintering method of 3D printing to prepare polysulfone membranes for oil-water separation. To impart increased hydrophobicity, the 3D-printed polysulfone membrane was surface-coated with candle soot by immersion, which resulted into a Janus-type membrane. The candle-soot treated membrane surface was superhydrophobic (161^{o} water contact angle, and 5^{o} water sliding angle), while the bottom (untreated) surface, was hydrophilic. Oil-water separation efficiency was maintained at 99% even after 10 cycles.

Most of the oil-water separation materials are polymer-based, thus when they are exposed to harsh conditions, they can degrade and lose their efficiency. In this situation, a ceramic-based material would be ideal. This inspired Chen et al. [62] to develop a 3D-printed ceramic-based (alumina) water-oil separation material functionalized on the surface with aluminium borate whiskers. The oil-water separation efficiency was >99% while maintaining high flowrate. Most interestingly, the prepared material showed high oil-water separation performance and durability even when exposed to harsh environments such as those solutions containing organic solvents, at high temperature and highly acidic condition. Their material showed better durability than metal or polymer-based counterparts. The final 3D printed material was easily optimized by simple high temperature heat treatment.

There has been increasing number of research using 3D printing to prepare sorbent materials for oil-water separation especially in the past three years. Aside from the rapid prototyping ability, 3D printing can also allow control of inner structure and surface, which definitely adds huge benefits for the sorbent's overall performance. This goes to show the promising approach to fabricate sorbent materials with user-defined and functional features. This include control of surface structure (e.g. roughness) that can generate superhydrophobic surface or oleophilic surface, though still limited on the printer resolution limits. Just like for a filter, the pore sizes or porosity needs of the sorbent materials may be a challenge for 3D printing if precision is needed going below one micron range. The kind of materials for 3D printing is still also rather limited especially for the specific properties needed for oil-water separation. In many cases, surface modification is still necessary in order to produce the desired surface characteristics. Polymers are still mostly used over ceramic ones especially as sorbents. Physical sorbents need some form of flexibility, in which polymeric materials can provide; though 3D-printed ceramic structure in the form of filter may be more advantageous in highly challenging environments. Another important aspect to consider for 3D-printed materials is the mechanical integrity of the sorption material. This also pertains to the robustness of interfacial bonding between the 3D printed material and the coating layer or nanoparticle inclusions as the sorbent will be subjected to challenging environments (highly acidic or alkaline) and various loadings (e.g., bending, squeezing for regeneration, etc.). As indicated in a previous study [18], the intrinsic property of the feedstock material before printing greatly affects the resulting mechanical property of the 3D-printed structure. In addition, the 3D-printing method and the build orientation are also two important factors on the resulting mechanical properties. An interesting direction for sorbent materials maybe towards smart sorbents via 4D printing, where multi-functionalities are provided on the sorbent as activated by an external stimuli such as pH, temperature, etc.

3.6. Solar absorbers for solar steam evaporation

Solar-driven water evaporation through utilizing solar illumination projected to photothermal materials has attracted tremendous attention in recent years as a potential solution for the shortage of clean water [94]. A good photothermal material for high efficiency solar steam evaporation (SSE) should possess the following: a broad light absorption over near infrared region (NIR), low thermal conductivity and a hydrophilic surface with open porous structures [95, 96]. In the past ten years, SSEs containing noble metals (e.g., Au, anodized aluminium oxide) and carbon materials (carbon nanotube (CNT) and graphene oxide (GO) e.g.) have been widely investigated. However, the main challenge for the technology is to fabricate easy-to-manufacture and scalable approaches, which can convert solar illumination into useable thermal energy with high energy efficiency. To address this challenge, researchers applied 3D printing technologies, enabling the prototyping and fabrication of photothermal materials with designed architecture and patterns for SSE applications with high energy efficiency. Vertical printing-based [97] and extrusion/direct ink writing-based [96] 3D printing techniques, appeared to be the most promising techniques for the design of 3D engineered materials with excellent properties and multi-functionalities for SSE. For instance, Yiju et al. [55] fabricated and designed a 3D-printed all-in-one evaporator with a concave structure that possessed a high porosity of 97.3% and an efficient solar absorption (>97%). The integrated SSE structure consisted of CNT/GO layer, GO/nanofibrillated cellulose layer (NFC), and GO/NFC wall. The as-designed materials achieved a solar steam generation efficiency of 85.6% under 1 Sun irradiation (1 kW m^{-2}), and obtained an evaporation rate of 1.25 $kgm^{-2} h^{-1}$. The authors attributed the performance to the low intrinsic thermal conductivity of porous evaporators, which facilitated heat localization and effectively minimized thermal dissipation to the bulk water.

In another study, 3D vertically-designed jellyfish-like evaporator was designed and fabricated by a vertical 3D printing technique [56]. It was prepared by printing a GO pillar vertically on a porous carbon black/GO layer (porosity~93%) (**Figure 10a**). The open porous structure of the evaporator absorbs high light within a wide optical absorption (250-2500 nm). In addition, the uniform distributed GO pillars was expected to decrease the horizontal water transport path length resulting in a sufficient water supply for steam generation. Furthermore, as described in **Figure 10b**, direct water pathways can significantly minimize the contact area between the illumination layer and bulk water, which can in turn prevent heat loss to the bulk water and further enhance steam generation efficiency. The addition of expanded polystyrene (EPS) foam thermal insulator plays a significant role in supressing heat dissipation to the bulk water. Therefore, the solar steam device showed an efficiency of 87.5% under 1-sun illumination. The ion concentration of Na^+, K^+, Mg^{2+} and Ca^{2+} of the seawater after purification were found to be far below the World Health Organisation (WHO) standards for drinking water.

He et al. fabricated freestanding 2D carbon nitride hybrid aerogel membrane with patterned macroscopic architecture using 3D printing [57]. The ink was prepared by mixing gold (Au) nanobipyramids, g-C_3N_4 nanosheets (Au/CNNS) dispersion and sodium alginate (SA) solution to increase the viscosity and obtain an optimum rheological behaviour for the smooth extrusion from a fine nozzle. Later on, the ink was printed on air, or into a reservoir of a $CaCl_2$/glycerol solution, or Pluronic F127. The as-printed structure exhibited broadband absorption in near infrared region (NIR) and an excellent solar light absorption. The as-obtained result was 2.5 times that of the baseline sample, which is attributed to the solution diffusion efficiency and liquid velocity of the 3D printed structure. Graphene inks are extensively studied for printed flexible electronics, because of their extraordinary high electronic conductivity and mechanical flexibility, as well as their chemical stability [98-101]. For example, Zhang et al, designed a 3D solar water heater housing self-supply model using 3D printing, composed of highly vertically ordered pillar arrays of graphene-assembled frameworks (HOPGF) (**Figure 10c and 10d**) [102]. It could potentially heat 30 Kg of water up to 50 ^oC with only one square meter of HOPGF under 1 sun within hours. They further demonstrated its practical application in a building with a roof area of 100 m^2, where large amount (480 kg) of water per day could be produced. This designed structure provided an efficient material for solar driven water treatment for practical applications. However, the cost of the materials is a main challenge and alternative low-cost carbon sources should be considered.

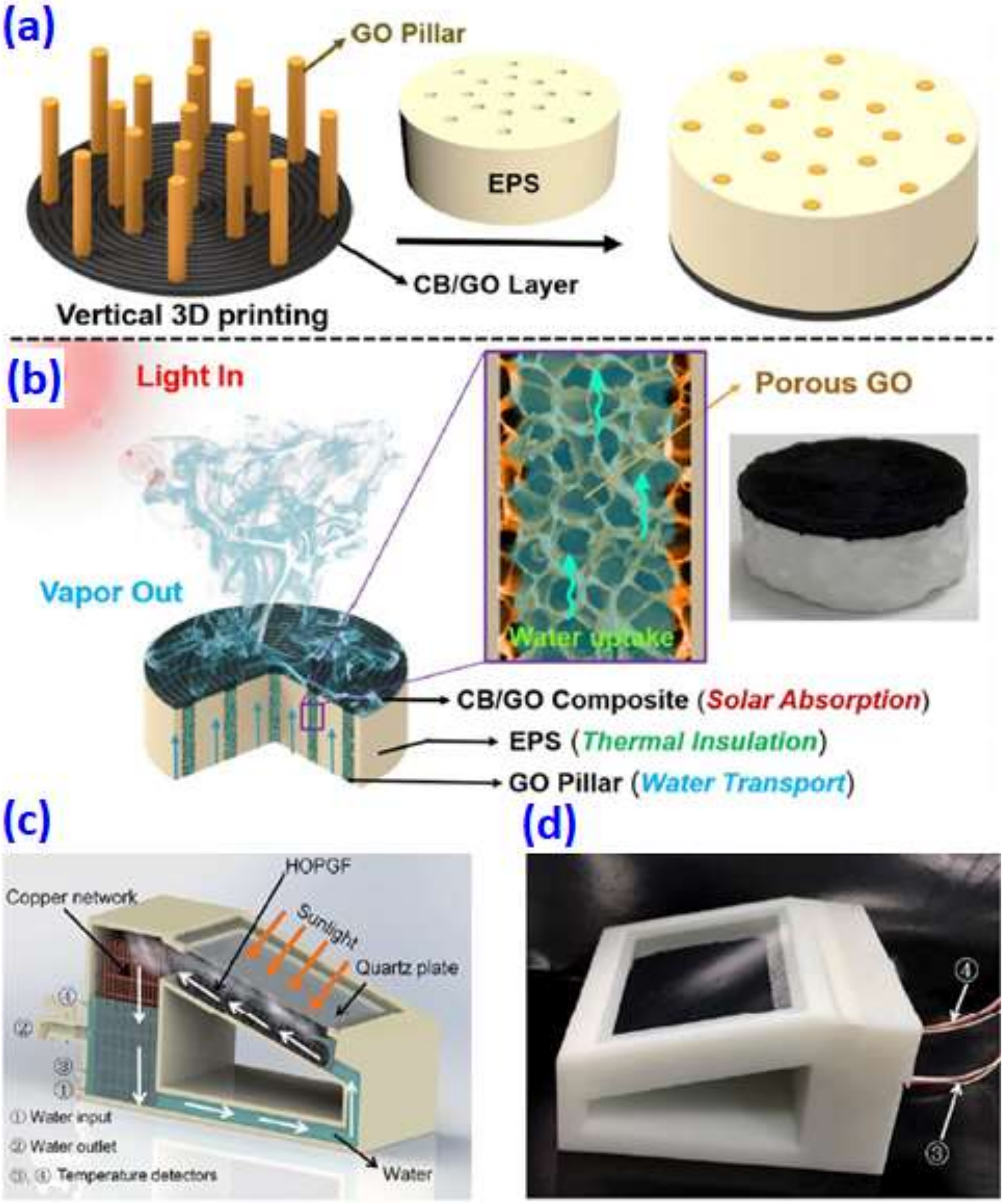

Figure 10. (a) Schematic describing the vertically-oriented 3D printed evaporator which is inserted in EPS foam; (b) principle illustration of the 3D printed evaporator and its corresponding photographic image [97]; (c) schematic illustration of the designed solar water heater system and (d) its corresponding photographic image [102].

3.7. Adsorbents/substrates for dye degradation

Carbon based materials are widely used as adsorbents for organic dye removal, however, the process of separation and recycling is intrinsically complicated. This is because the materials are in powder form thus have a lack of flexibility [103, 104]. The 3D printing process provides flexible materials with porous and open structures that can directly adsorb organic dyes with high efficiency, and can potentially be recycled. One of the promising materials for many different applications is metal organic frameworks (MOFs), which possess porous crystalline structures, open channels and large surface areas, composed of several functional groups [58, 105]. These inherent features provide a promising material with wide applications such as the removal of organic dyes. To enhance the flexibility of MOF, Wang et al. utilized 3D printing for the fabrication of acrylonitrile butadiene styrene (ABS) coated with porous Cu-Benzene tricarboxylic acid adsorbents for methylene blue (MB) removal [58]. The preparation process involves the coating of Cu-BTA onto a 3D printed ABS surface. The Cu-BTC/ABS composite enhances surface wettability, which in turn helps to enhance the adsorption of metals and linkers. The composite was designed in a variety of number shapes (**Figure 11a**). The SEM images reveal that the printed composite exhibited a smooth surface with some small hills. MB removal efficiency of 93.3% and 98.3%, for solution with concentrations of 10 and 5 mg/L, respectively, was achieved within 10 min. **Figure 11b** illustrates that the composite could be recycled without any complications displaying its promising practical application.

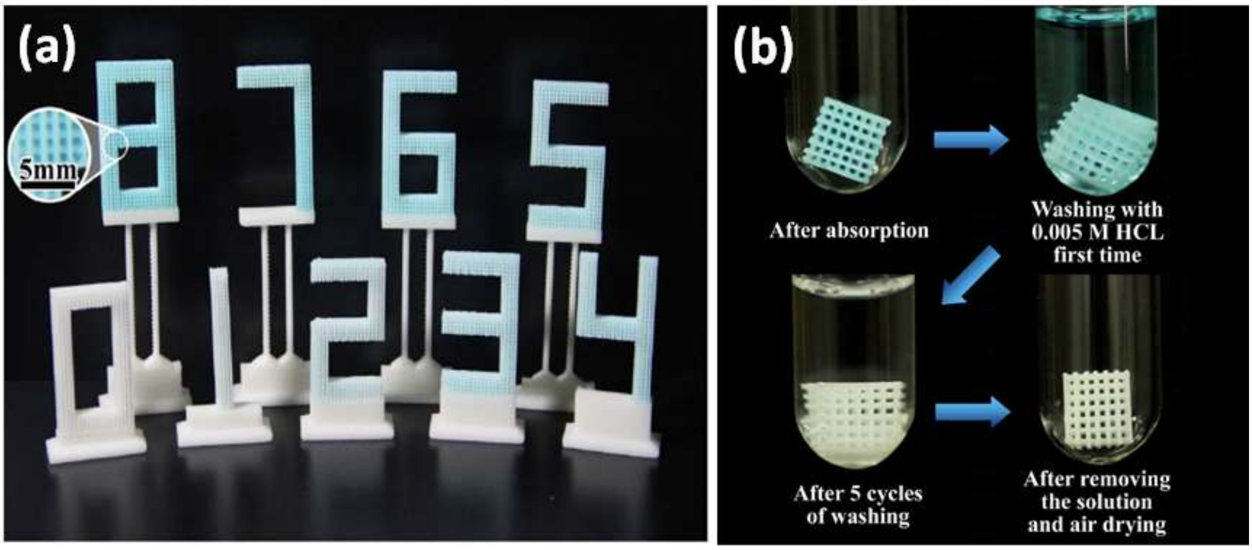

Figure 11. (a) Photographs of the synthesized Cu-BTC/ABS composites (the printed number illustrates the number of cycles); (b) Photos of the recycling process of ABS polymer skeleton. (adapted from [58]).

In contrast, Figuerola and his co-workers incorporated sub-micrometric crystals of a Zeolitic Imidazole Framework (ZIF-67)/ polymer mixed matrix on 3D printed device though a sample coating process [59]. The device was used for the degradation of Rhodamine B as a model dye. The 3D-coated device exhibited an average degradation of 97-98% after 10 cycles with excellent reproducibility and reusability. Liu et al. used a direct ink writing (DIW) 3D printing to fabricate nitrogen-doped carbon materials with different mesopores/microspores and monolithic structures with surface area of 816 m^2g^{-1}. The ink was prepared by adding melamine, which acts as a nitrogen source to the starch gelatin system, and SiO_2 as a template. Freeze-drying and carbonization steps were done after 3D printing, while the template was removed via etching method. The printed monolithic structures showed an excellent adsorption of MB dyes. Further, the materials can be recycled without any complicated process.

Adsorbent materials or substrates for dye degradation need high surface area to enhance the adsorption sites and efficiency. Moreover, for practical application, mechanical stability for cyclic use of the adsorbent is an important requirement. In many cases, adsorbent materials are changed by modifiers (bio-based or inorganic modifiers such as CNTs, clay, etc.) by mixing or coating. However, there is high possibility of poor adhesion of coating layer or modifiers to the 3D-printed substrate, which could thereby lead to delamination and potentially cause secondary pollution. Challenge still remains on the ability of the current 3D printer to follow the exact CAD model at the highest resolution, i.e., achieving the micro to nano-level roughness which supposedly can increase the surface area is still unachievable. Efforts in the future should focus on enhancing the adhesion between fillers and polymer matrix, and improving the current print-head designs of 3D printers (e.g., FDM) that would allow less or no pre-processing or mixing.

3.8. Adsorbents for heavy metal adsorption

The removal of heavy metals from water including copper, lead, cadmium and mercury has received considerable attention due to their toxicity. These toxic metals have severe detrimental effects on human health via accumulation through the living organism [106, 107]. Therefore, a scalable and sufficient method to remove these toxic metals is essential for the safety of the public. Adsorbents such as activated carbon, carbon nanotubes, bio-inspired materials, and other porous carbon materials have been proposed for the removal of heavy metals through a porous media. Prominent is the use of bio-inspired materials, due to its intrinsic advantages of low-cost, effectiveness and biodegradability [108, 109]. Chitosan is an example of a biocompatible material, which can adsorb heavy metals, but it suffers from poor reusability and processability. 3D printing overcomes the issues through designing 3D structures that possess a porous structure and a large surface area, as well as potential reusability. For instance, Zhang et al. designed bio-adsorbents consisting of monolithic 3D porous chitosan composite adsorbing filter via a stereolithography-based 3D printing technique and applied it for Cu removal [108]. Several structures were designed such as closely arranged hexagonal holes, round holes, square holes and skewed hexagonal holes. **Figure 12a** reveals the composite with skewed hexagonal holes and emerged as the most efficient structure with a high adsorption. The reusability was investigated by an adsorption-desorption test with an aqueous ethylenediaminetetraacetic acid (EDTA) solution as the eluent. Around 92% desorption capacity was achieved and the value remained constant throughout the process proving its reusability. The authors only limited the applications to Cu(II) removal. The application of 3D printing was further expanded to generate materials with a unique structure. For instance, hydrogel materials (**Figure 12b**) were considered as heavy metal adsorbents, because of its advantages of having open porous structure with a large surface area. For example, extrusion based 3D printing was applied to fabricate 3D hydrogel structures for heavy metal ion removal (Cu^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+})[109]. The hydrogel was prepared by mixing chitosan and diacrylated Puronic F-127 (F127-DA) at different ratios. The results showed that the printability of chitosan reduced as the concentration of chitosan increased. The hydrogel with structural features adsorbed up to 95% of metals within 30 min.

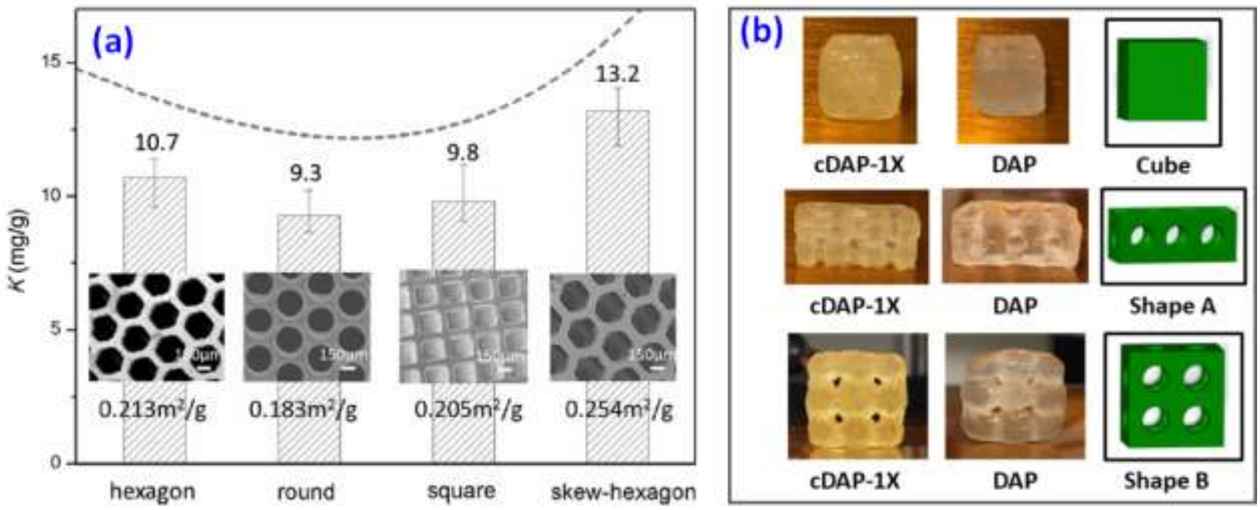

Figure 12. (a) Comparative illustration of the adsorption capacity for Cu(II) of chitosan-based 3D-printed filters with varying designs (T=25 °C, pH 5.5) [108]; (b) 3D-printed hydrogels used for removal of different heavy metals (Cu^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}) [109].

For heavy metal removal, 3D printing provides an exciting avenue to create materials in various forms and shapes with ease of preparation, may it be as hydrogels, filters, sorbents, etc. regardless of the complexity of the design. The specific surface area is an important parameter for adsorption processes, thus enabling precise design and manufacture of internal structure by 3D printing definitely is an advantage for such an application. 3D printing is also an approach for a "greener" fabrication of chitosan-based adsorbent membranes for heavy metal removal. Instead of using large amounts of solvents and acids/bases to process chitosan, a facile way is to directly 3D-print (by SLS) chitosan mixed with thermoplastic polyurethane (TPU) for a solvent-less membrane fabrication method [110]. Cu(II) and Pb(II) were efficiently adsorbed on the membrane. In recent years, chitosan-based hydrogels have been increasingly investigated using 3D-printing due to the ability of hydrogel to respond quickly with external stimuli with reversible volume changes (this is essentially 4D printing). 3D printing can either be used to directly print the sorbent material, print the substrate for which it is functionalized with sorptive properties, and print the template for which sorbent material is molded. All these approaches provide precision-3D-printing of any geometrical shapes and structures that are otherwise very difficult to achieve by conventional fabrication technique. Making composite 3D-printed material decorated with heavy-metal binding sites is also a good strategy, but issues on defects due to nanofiller content especially when using thermoplastic polymers are a concern [105]. The nanofillers can induce void formation thereby affecting the overall mechanical integrity of the 3D-printed structure.

4. Challenges of 3D printing

4.1. Material and process limitations

a. **Resolution/accuracy** - Limited resolution or layer height: This limitation is a particular disadvantage for the direct fabrication of membranes, where layer height and pore sizes of most membranes are in the sub-micrometer level. The further development of the two-photon polymerization which could print to a very high resolution of ~100 nanometers would potentially be able to address this issue [111]. Many of the available 3D printers and 3D printing technologies today have issues regarding accuracy/precision of printed parts in comparison with the 3D model, and needs to be redesigned and reprinted for a more accurate part (i.e. perfect fit).

b. **Limited types of applicable 3D printing materials available/performance-** Adding more types of 3D printing materials is needed (especially those being used for conventional membrane production such as polyvinylidende fluoride (PVDF), polypropylene, polytetrafluoroethylene (PTFE), polyimide, polyamide, polyethersulfone, polyetherimides, etc; simultaneous printing of multiple materials having different properties and functions would also advance the adoption of 3D printing technologies for membrane design and fabrication. The material used and the 3D printing technique also dictate the resulting properties and performance of the 3D-printed part. Mechanical strength is an important paramater and 3D-printed materials should be able to withstand high amounts of pressure under various challenging environments. This is especially true when dealing with wastewater or saline water where the pH level may be extreme or there are various impurities in the solution. There are certain types of polymers (e.g. photopolymers) that undergo swelling when soaked in water due to its hydrophilic behavior [112]. In some materials, this could affect the structural integrity of the printed part. Proper selection of photopolymer and photoiniator is crucial when using the SLA-AM technology. Also, in some cases, the solution may degrade (especially) the polymer materials.

c. **Slow printing speed / Poor scalability / Need for post-processing-** 3D printing is a highly customizable but slow process. Printing a large piece with high resolution could take a very long time to finish. New 3D printing technologies such as the CLIP process could potentially solve this issue [113]. Limited build size: 3D printers should be able to print at least 1 meter in width to enable fast production and upscaling especially if preparing membranes. The staircase effect is an example of an inherent characteristic of 3D-printed parts which needs post-processing. SLS - AM produces rough surfaces, which could either be advantageous or disadvantageous to membrane design especially on its effect on the fouling/antifouling properties [114].

d. **Cost-** 3D printing is still relatively more expensive than many other conventional and formative fabrication techniques due to material requirement and fabrication times, and most especially when compared to conventional membrane fabrication techniques. For example, for FDM printing using ABS material (commercial-grade), it can cost around US$250 per kilogram, or for stereolitography, >US$200 per kilogram for photopolymers [13]. This does not take into account the lost or unused material after printing. There is a need to significantly reduce the cost of printing materials, technologies and processes (e.g. laser-based technologies consume relatively more power/energy during operation).

4.2. Safety and environmental concerns of 3D printing

While it is true that 3D printing has greatly revolutionized the manufacturing technology, there are some environmental impacts and safety concerns that need to be addressed. One of the hazards of 3D printing processes is the particulate emission, such as ultrafine particle emission (UFP) and volatile organic compound (VOC) emission, from the materials being used. According to Azimi et al., UFP emission rate is highest when using ABS and polycarbonate filaments, and lowest at PLA and other filaments such as nylon. The individual VOC emission rate is highest among nylon-based, laywood and laybrick filaments, ABS, and high-impact polysterene (HIPS) filaments. Until a low-emitting filament is designed to reduce the UFP and VOC concentrations, it was suggested to avoid working on 3D printers in an enclosed space with poor ventilation or without gas and particle filtration system [115].

Kim et al. reported that FFF printers emit high concentrations of nano-size particles including carcinogenic formaldehydes, phthalates and some VOCs such as toluene and ethylbenzene [116]. In SLS printing, operators can have significant exposure to polymer or metal particles when handling powders [117]. Moreover, solvent baths are sometimes used in FFF and SLS prints in order to remove the supports or to improve the surface quality. For postprocessing of DLP and SLA prints, alcohols or propylene carbonate are used when removing the residual resins [118]. These solvents can be toxic to humans and environment if not properly handled.

Studies on life cycle assessment (LCA) were conducted to identify the human health risks and environmental as well as ecological impacts of 3D printing technology from material sourcing and handling to printing process and waste disposal. Faludi et al. concluded that the sustainability of 3D printers depends mainly on the proper utilization of machines to reduce the idling energy and to be more efficient in electricity usage. The energy demand during printing process dominates the environmental impacts of 3D printing technology [119]. The environmental burdens and health hazards can be minimized through these assessments and by optimizing and improving the 3D printing processes.

4.3. Industrial upscaling challenges and potential of 3D printing

Additive manufacturing (or 3D printing) is still at its growing stage and still faces many challenges especially for industrial upscaling. However, the tide could potentially change anytime soon with the provision of more powerful and bigger 3D printers, wider range of new feed stock materials, and new way of measurement and product quality control. There is significant interest from industry to adopt the AM technology in their processes, and in fact, AM has already shifted from prototyping to production. Using 3D printing, production of parts on demand (i.e. produce-to-order) would enable manufacturers to print parts as needed instead of producing-to-stock. This could significantly reduce inventory and storage costs. Distributed manufacturing, which is the manufacturing of the product closer to customers, is also made possible by 3D printing (which is a form of digital manufacturing). Essentially, 3D CAD files will be sent to smaller sites or remote locations. Also, development of materials for specific applications is very important for industrial applications. Specifically, development of 3D printing materials that are cheaper, stronger, more lightweight, more environment-friendly are important research topics for the adoption of 3D printing for industrial applications. Customization for industrial applications would be vital especially for rapid parts replacement (of hard to find parts) [120]. Currently, 3D printing is more suitable to high value (complex design) low volume products compared with traditional manufacturing wherein economies of scale is an important consideration to recover cost. The adoption of 3D printing to industrial applications at this stage is more geared towards producing parts that are impossible or more expensive if conventional manufacturing is used [121].

A number of companies have slowly adopted the use of 3D printing in their processes. For example, Adidas, in partnership with Carbon, printed high quality midsoles for sneakers. Carbon uses high-performance/precision LED light (Digital Light Synthesis Technology) that projects images of the cross-sectional areas of the parts. BMW is using the powder-based selective laser melting (SLM) technology to make mountings for the top cover of the roof mechanism (opening/closing). Rehook, developed by cyclists, is a tool, which helps reattach dropped bike chain back on track. Designers use graphite-filled nylon material and SLS 3D printers. With these examples, it can be said that 3D printing is now getting ready for mass production, however, the cost and complexity of part (design) will play a big role in determining whether to choose traditional way of manufacturing (i.e. subtractive manufacturing and formative manufacturing) or additive manufacturing (i.e. 3D printing) [122]. Serial production, which is one type of mass production, is used in the production of items in series made in the same way. FDM printing is now poised to be used in serial production due to its cost and ease of production. 3D printing farm, which is a collection of 3D printers arranged alongside each other can be an approach for mass production of parts, with the objective of on-demand and efficient manufacturing. However, the initial cost and maintenance will be an issue. Many companies have recently joined the race in creating large-scale printers (print dimension exceeding 1 m) to offer to the market.

One of the main challenges in adopting 3D printing for industry use is the functionality of the part, which is very much related to how it is used by the market. An important consideration also is the behavior of the parts during its use (operation) which is related to its properties (metrology – pertaining to real time quality measurements), for example mechanical properties when used for structural applications. Of course ultimately, the cost should be considered [121]. Another important factor is the software used and the techniques and skills to optimize the use of available computer programs. One issue is on designing the part including the support and internal structures. Another consideration is the development of user-friendly software. The goal of software developers is to decrease the expert knowledge needed by users to 3D print. In connection to this, the development of an operating system which could be adopted by all 3D printer OEMs, similar with the Microsoft Windows Operating System. Generative Design, which is an iterative design method involving a computer program that generates several outputs meeting certain real-world constraints, should also be considered [123].

The potential of 3D printing in the future seems to be unlimited if all the challenges are addressed. The expectation is that there will be more spin-off innovative and exciting applications that will come in the long term due to more precise 3D printers at lower cost, new materials, and high quality automated control from pre-processing until post-processing.

5. Future prospects

5.1. Combination of 3D printing + other processes

A potential future direction of 3D printing may be one that is not entirely a stand-alone process but more of integrated multi-process system, by its combination with other manufacturing processes. This is particularly true for membrane fabrication for desalination and membrane separation processes, as the 3D printing resolution is not yet able to directly print the entire membrane at the resolution needed. Therefore, a combination of conventional active layer fabrication and 3D printed middle or support layer would be attractive as already demonstrated by a few recent studies.

5.1.1. 3D printing + electrospinning/spraying or solution blow spinning

One way of combining two processes to fabricate a composite membrane is the combination of 3D printing and electrospinning. This is interesting for membrane preparation for water treatment as the 3D printed support layer can be designed and fabricated with high porosity, while the active layer can be made from ultrafine electrospun nanofibers where pore sizes can be easily tailored. This type of nanofiber/3D printed layer combination has been actively researched in the biomedical filed, but not yet in the water treatment field. For example, Lee et al. [124] combined electrospinning and 3D bioprinting in the preparation of a bio-tubular scaffold used for the fabrication of artificial vascular graft. Surface morphology and mechanical properties increased using this hybrid method. Rajzer et al. [125] also combined 3D printing and electrospinning in creating a multifunctional layered scaffold for subchondral bone reconstruction and nasal cartilages. The mechanical properties of 3D-printed scaffolds with varying internal architecture were tested. Naghieh et al developed hierarchical scaffolds using FDM 3D-printed micro struts (using polylactic acid – PLA) and electrospun nanocomposite fibrous layers (using gelatin-forsterite) and concluded it can be used for bone tissue regeneration [126]. The main issue with composite membrane approach is the delamination possiblity at the interface layer of the nanofiber and the 3D printed membrane.

In relation to membrane and module preparation, there is a need for validation of different membrane designs with computational fluid dynamics (CFD) [3]. As accurate simulations of some parameters are not possible using CFD [44], employing additive manufacturing in rapid prototyping and rapid validation would be very important. Lee et al [3] added that CFD analyses may be combined with additive manufacturing in validating complicated geometries. With module casings, feed spacers and other related module parts having dimensions above the millimeter scale, additive manufacturing is now being adopted for the design and protyping of these components.

5.1.2. Hybrid manufacturing combining additive manufacturing with subtractive manufacturing and formative manufacturing

There is a potential synergistic effect of hybridizing additive manufacturing with other conventional manufacturing techniques. The process can start with the 3D printing (additive manufacturing) of injection molds, and then followed by injection molding (formative manufacturing) of material (e.g. plastic) onto the mold, and lastly employing subtractive manufacturing (e.g. drilling, milling, etc) to add or enhance some features, as well as to do finishing/post-processing. Hybrid manufacturing using 3D-printed molds has several advantages, such as [127]:

1) Fast launching: 3D printing of molds usually just takes a few days to conceptualize, and several hours to print.
2) On-demand fabrication: easy correction/redesign of molds is possible.
3) Cost-effective production: 3D-printed molds are cheaper than molds fabricated using conventional mold fabrication.
4) Freedom of geometry design: complex designs are easier to build using 3d printing compared with traditional tooling process.

This could be potentially implemented for bigger parts needed such as modules for solar water evaporation, membrane modules, and templates for hydrogels for adsorption. This would not be ideal for very thin parts such as membranes due to inaccuracy concern, thereby relating to product quality as well. Another hybrid technology is similar with the Large Additive Subtractive Integrated Modular Machine (LASIMM). It has additive and subtractive manufacturing capabilities. Specifically, it has additive manufacturing, cold-work, machining, metrology and inspection capabilities [128].

5.2. 4D printing

Another exciting research direction would be by 4D printing approach to fabricate materials for water-related applications**.** 4D printing is an “upgrade” of 3D printing, adding the element of time, i.e., the property, function or shape of a 3D-printed part can change as a function of time [30] (see differences in **Fig. 13**). This makes the 3D printed object “alive” by exposure to external stimuli. Examples of such transformation/shifting include bending, folding, twisting, surface curling, linear or nonlinear expansion, and surface generation (e.g., wrinkles, buckles and creases) either from 1D, 2D, 3D structures or their combination [129]. With 4D printing, multi-functionality, self-assembly, reconfiguration, replication and self-repair is possible. Thus, this provides certain advantages such as reduction of volume for storage, and shape transformations which is possible with flat-pack 3D-printed structures. 4D printed structures can see major applications in medicine, space, satellites, construction, architecture, sensing and actuation, and in membrane separation [129]. Shape-shifting materials are mainly two types, namely, shape-memory materials and shape changing materials which are extensively discussed previously [129, 130]. This is possible with the right combination of smart (e.g. active expandable polymer) and conventional (e.g. rigid plastic) materials [131, 132], stimulus, interaction mechanism, mathematical modelling, as well as with the appropriate printing technology. Appropriate materials are usually those which could swell or expand. Specifically, characteristics of smart materials include shape memory, responsiveness, and multifunctionality among others. Further, previous reports showed different material classifications, for example single-material or multimaterial structures; other groups classified the materials as composite materials, discrete multiple materials and porous materials [133]. Further, other groups classified under digital materials and further categorized as uniform distribution, gradient distribution, and special patterns; another one is structures with and without hinges and joints.

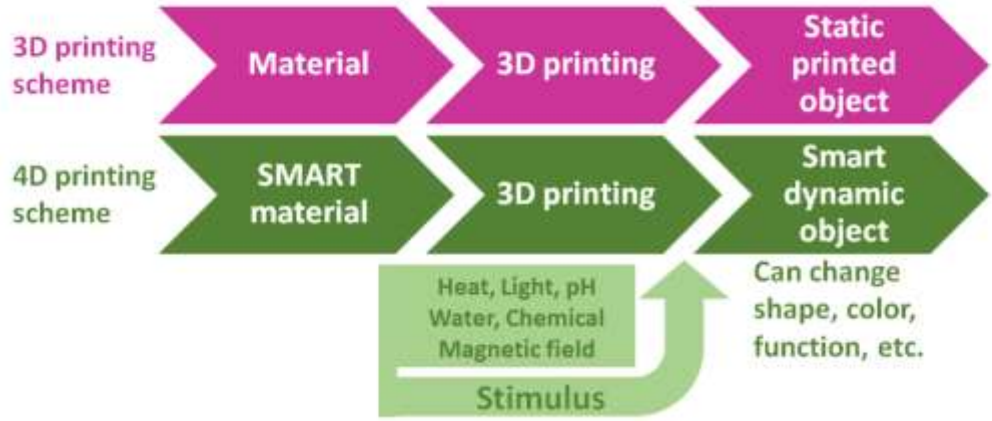

Figure 13. Differences between 3D printing and 4D printing processes and the capability of the printed objects. For 4D printed structures, the printed objects come “alive” upon exposure to various stimuli. (modified from [129])

The important consideration for using materials are printability and intelligence. 3D printing technologies used include FDM, mask-image-projection-based stereolithography, high resolution microstereolithography with automated material exchange mechanism, and direct-write printing, etc. Stimuli include heat, light, water or various combinations of all these. Examples of interaction mechanisms include constrained thermo-mechanics [134], unconstrained thermo-mechanics [135], unconstrained hydro-mechanics [131, 132], unconstrained hydro-thermo-mechanics [136], unconstrained thermo-photo-mechanics [137], osmosis-mechanics [138], dissolution mechanics [139], and unconstrained-pH-mechanics [140]. Mathematical modelling is needed in order to predict the shape-shifting of the material/s, to reduce the number of experiments (trial and error), and to prevent collisions of components during shape-shifting. Inputs to mathematical models include the shape, material properties, material structure and stimulus properties [129]. Matthews et al. [141] reported the 3D printing of acrylic polymer containing biological materials, i.e. membrane proteins using a DLP 3D printer. The fourth dimension is the bio functionality of these proteins. The authors reported on the 4D printing of a bio-inspired nano hybrid electrode for water-splitting applications. They use a polymeric resin with proton-pumping bacteriorhodopsin (bR), carbon nanotubes (CNT), and silver nanoparticles (Ag NP). The authors claimed that “these printed photo electrochemical cells exhibit high durability, low onset over potential, and upon light irradiation (535 nm) produces hydrogen by a synergistic effect of Ag NP and bR” [141]. Miao et al reviewed several applications of 4D printing in membrane applications, examples are those using light and heat as stimuli [142]. In particular interest is the 4D printing of smart membranes, where the pores of the membranes can close or open, or the surface wettability can turn into hydrophilic or hydrophobic, depeding on the external stimuli applied such as temperature change, pH change or some other parametric/stimuli changes.

6. Conclusion

3D printing technology presents a high potential for use in various prototyping and fabrication processes including water-related applications. It is fast, versatile and efficient, which can fabricate virtually any shape and geometry enabling a new paradigm in the manufacturing industry. This review presented an overview of exciting developments in 3D-printed materials in the water-related field including preparation and use of feed channel spacers, membranes, solar absorbers, bio-carriers for wastewater treatment, adsorbents for oil-water separation and heavy metal treatment, desalination, among others. It is emphasized that in most water-related applications with macro-level materials (>1 um range), the use of 3D printing is most suitable as it offers more degrees of freedom in design. However, those needing below 1 um range resolution are still facing challenges in precision fabrication of materials especially on direct printing of membranes. Key areas that need to be further investigated and improved are on the printing resolution/accuracy, applicability of various materials for printing, printing speed and scalability, and the total cost of the process. The exciting hybridization of 3D printing with other fabrication processes may allow production of more novel designs and functionalities. Making the 3D printed material to be responsive to stimuli via 4D printing will open new horizons of research and further applications. Overall, the exciting field of 3D printing as a manufacturing technique is a new paradigm in new material design and fabrication that have wide promise in water-related applications. There is already a drastic advancement in the last few years in 3D printing, however, some 3D printing material, process, cost and post-processing parameters and even its environmental and health impacts needs to be addressed in order to fully realize its unlimited potential.

Conflict of interest

Authors hereby confirm that this manuscript has not been published and is not under consideration elsewhere. Authors declare no conflict of interest.

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References

[1] P.J.J. Alvarez, C.K. Chan, M. Elimelech, N.J. Halas, D. Villagrán, Emerging opportunities for nanotechnology to enhance water security, Nature Nanotechnology 13(8) (2018) 634-641.

[2] T.D. Ngo, A. Kashani, G. Imbalzano, K.T.Q. Nguyen, D. Hui, Additive manufacturing (3D printing): A review of materials, methods, applications and challenges, Composites Part B: Engineering 143 (2018) 172-196.

[3] J.-Y. Lee, W.S. Tan, J. An, C.K. Chua, C.Y. Tang, A.G. Fane, T.H. Chong, The potential to enhance membrane module design with 3D printing technology, Journal of Membrane Science 499 (2016) 480-490.

[4] J.-Y. Lee, J. An, C.K. Chua, Fundamentals and applications of 3D printing for novel materials, Applied Materials Today 7 (2017) 120-133.

[5] M.L. Perrotta, G. Saielli, G. Casella, F. Macedonio, L. Giorno, E. Drioli, A. Gugliuzza, An ultrathin suspended hydrophobic porous membrane for high-efficiency water desalination, Applied Materials Today 9 (2017) 1-9.
[6] F. Li, W. Meindersma, A.B. de Haan, T. Reith, Novel spacers for mass transfer enhancement in membrane separations, Journal of Membrane Science 253(1) (2005) 1-12.
[7] N. Sreedhar, N. Thomas, O. Al-Ketan, R. Rowshan, H. Hernandez, R.K. Abu Al-Rub, H.A. Arafat, 3D printed feed spacers based on triply periodic minimal surfaces for flux enhancement and biofouling mitigation in RO and UF, Desalination 425 (2018) 12-21.
[8] N. Thomas, N. Sreedhar, O. Al-Ketan, R. Rowshan, R.K. Abu Al-Rub, H. Arafat, 3D printed spacers based on TPMS architectures for scaling control in membrane distillation, Journal of Membrane Science 581 (2019) 38-49.
[9] N. Yanar, M. Son, E. Yang, Y. Kim, H. Park, S.-E. Nam, H. Choi, Investigation of the performance behavior of a forward osmosis membrane system using various feed spacer materials fabricated by 3D printing technique, Chemosphere 202 (2018) 708-715.
[10] T. Femmer, A.J.C. Kuehne, J. Torres-Rendon, A. Walther, M. Wessling, Print your membrane: Rapid prototyping of complex 3D-PDMS membranes via a sacrificial resist, Journal of Membrane Science 478 (2015) 12-18.
[11] L.C. Hwa, M.B. Uday, N. Ahmad, A.M. Noor, S. Rajoo, K.B. Zakaria, Integration and fabrication of the cheap ceramic membrane through 3D printing technology, Materials Today Communications 15 (2018) 134-142.
[12] A. Al-Shimmery, S. Mazinani, J. Ji, Y.M.J. Chew, D. Mattia, 3D printed composite membranes with enhanced anti-fouling behaviour, Journal of Membrane Science 574 (2019) 76-85.
[13] Z.-X. Low, Y.T. Chua, B.M. Ray, D. Mattia, I.S. Metcalfe, D.A. Patterson, Perspective on 3D printing of separation membranes and comparison to related unconventional fabrication techniques, Journal of Membrane Science 523 (2017) 596-613.
[14] L. Hu, G. Jiang, 3D Printing Techniques in Environmental Science and Engineering Will Bring New Innovation, Environmental Science & Technology 51(7) (2017) 3597-3599.
[15] H.A. Balogun, R. Sulaiman, S.S. Marzouk, A. Giwa, S.W. Hasan, 3D printing and surface imprinting technologies for water treatment: A review, Journal of Water Process Engineering 31 (2019) 100786.
[16] I.A. 52915:2016, I. 261 A. Manufacturing, https://www.iso.org/standard/67472.html Accessed: 23-Jun-2019 (2016).
[17] A.C. de Leon, Q. Chen, N.B. Palaganas, J.O. Palaganas, J. Manapat, R.C. Advincula, High performance polymer nanocomposites for additive manufacturing applications, Reactive and Functional Polymers 103 (2016) 141-155.
[18] J.R.C. Dizon, A.H. Espera, Q. Chen, R.C. Advincula, Mechanical characterization of 3D-printed polymers, Additive Manufacturing 20 (2018) 44-67.
[19] A.H. Espera, J.R.C. Dizon, Q. Chen, R.C. Advincula, 3D-printing and advanced manufacturing for electronics, Progress in Additive Manufacturing (2019).
[20] K. Gnanasekaran, T. Heijmans, S. van Bennekom, H. Woldhuis, S. Wijnia, G. de With, H. Friedrich, 3D printing of CNT- and graphene-based conductive polymer nanocomposites by fused deposition modeling, Applied Materials Today 9 (2017) 21-28.
[21] M. Vaezi, H. Seitz, S. Yang, A review on 3D micro-additive manufacturing technologies, The International Journal of Advanced Manufacturing Technology 67(5) (2013) 1721-1754.
[22] X. Wang, M. Jiang, Z. Zhou, J. Gou, D. Hui, 3D printing of polymer matrix composites: A review and prospective, Composites Part B: Engineering 110 (2017) 442-458.
[23] S. Crump, Fast, Precise, Safe Prototype with FDM, ASME PED 50 (1991) 53-60.
[24] A.K. Sood, R.K. Ohdar, S.S. Mahapatra, Parametric appraisal of mechanical property of fused deposition modelling processed parts, Materials & Design 31(1) (2010) 287-295.
[25] A. Tsouknidas, Friction Induced Wear of Rapid Prototyping Generated Materials: A Review, Advances in Tribology 2011 (2011) 7.
[26] J.M. Williams, A. Adewunmi, R.M. Schek, C.L. Flanagan, P.H. Krebsbach, S.E. Feinberg, S.J. Hollister, S. Das, Bone tissue engineering using polycaprolactone scaffolds fabricated via selective laser sintering, Biomaterials 26(23) (2005) 4817-4827.

[27] S. Kumar, J.-P. Kruth, Wear Performance of SLS/SLM Materials, Advanced Engineering Materials 10(8) (2008) 750-753.
[28] G.D. Kim, Y.T. Oh, A benchmark study on rapid prototyping processes and machines: Quantitative comparisons of mechanical properties, accuracy, roughness, speed, and material cost, Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture 222(2) (2008) 201-215.
[29] C. Deckard, J.J. Beaman, Process and control issues in selective laser sintering, American Society of Mechanical Engineers, Production Engineering Division (Publication) PED, 1988, pp. 191-197.
[30] I. Gibson, Material properties and fabrication parameters in selective laser sintering process, Rapid Prototyping Journal 3(4) (1997) 129-136.
[31] N. Thomas, N. Sreedhar, O. Al-Ketan, R. Rowshan, R.K. Abu Al-Rub, H. Arafat, 3D printed triply periodic minimal surfaces as spacers for enhanced heat and mass transfer in membrane distillation, Desalination 443 (2018) 256-271.
[32] E.H.C. Castillo, N. Thomas, O. Al-Ketan, R. Rowshan, R.K. Abu Al-Rub, L.D. Nghiem, S. Vigneswaran, H.A. Arafat, G. Naidu, 3D printed spacers for organic fouling mitigation in membrane distillation, Journal of Membrane Science 581 (2019) 331-343.
[33] W.S. Tan, C.K. Chua, T.H. Chong, A.G. Fane, A. Jia, 3D printing by selective laser sintering of polypropylene feed channel spacers for spiral wound membrane modules for the water industry, Virtual and Physical Prototyping 11(3) (2016) 151-158.
[34] W.S. Tan, S.R. Suwarno, J. An, C.K. Chua, A.G. Fane, T.H. Chong, Comparison of solid, liquid and powder forms of 3D printing techniques in membrane spacer fabrication, Journal of Membrane Science 537 (2017) 283-296.
[35] A. Siddiqui, N. Farhat, S.S. Bucs, R.V. Linares, C. Picioreanu, J.C. Kruithof, M.C.M. van Loosdrecht, J. Kidwell, J.S. Vrouwenvelder, Development and characterization of 3D-printed feed spacers for spiral wound membrane systems, Water Research 91 (2016) 55-67.
[36] Y.Z. Tan, Z. Mao, Y. Zhang, W.S. Tan, T.H. Chong, B. Wu, J.W. Chew, Enhancing fouling mitigation of submerged flat-sheet membranes by vibrating 3D-spacers, Separation and Purification Technology 215 (2019) 70-80.
[37] S. Kerdi, A. Qamar, J.S. Vrouwenvelder, N. Ghaffour, Fouling resilient perforated feed spacers for membrane filtration, Water Research 140 (2018) 211-219.
[38] J. Balster, I. Pünt, D.F. Stamatialis, M. Wessling, Multi-layer spacer geometries with improved mass transport, Journal of Membrane Science 282(1) (2006) 351-361.
[39] A. Shrivastava, S. Kumar, E.L. Cussler, Predicting the effect of membrane spacers on mass transfer, Journal of Membrane Science 323(2) (2008) 247-256.
[40] J. Liu, A. Iranshahi, Y. Lou, G. Lipscomb, Static mixing spacers for spiral wound modules, Journal of Membrane Science 442 (2013) 140-148.
[41] C. Fritzmann, M. Hausmann, M. Wiese, M. Wessling, T. Melin, Microstructured spacers for submerged membrane filtration systems, Journal of Membrane Science 446 (2013) 189-200.
[42] C. Fritzmann, M. Wiese, T. Melin, M. Wessling, Helically microstructured spacers improve mass transfer and fractionation selectivity in ultrafiltration, Journal of Membrane Science 463 (2014) 41-48.
[43] S.M. Ali, A. Qamar, S. Kerdi, S. Phuntsho, J.S. Vrouwenvelder, N. Ghaffour, H.K. Shon, Energy efficient 3D printed column type feed spacer for membrane filtration, Water Research 164 (2019) 114961.
[44] S. Badalov, Y. Oren, C.J. Arnusch, Ink-jet printing assisted fabrication of patterned thin film composite membranes, Journal of Membrane Science 493 (2015) 508-514.
[45] S. Mazinani, A. Al-Shimmery, Y.M.J. Chew, D. Mattia, 3D Printed Fouling-Resistant Composite Membranes, ACS Applied Materials & Interfaces (2019).
[46] Y. Chen, P. Gao, M.J. Summe, W.A. Phillip, N. Wei, Biocatalytic membranes prepared by inkjet printing functionalized yeast cells onto microfiltration substrates, Journal of Membrane Science 550 (2018) 91-100.
[47] M. Singh, A.P. Haring, Y. Tong, E. Cesewski, E. Ball, R. Jasper, E.M. Davis, B.N. Johnson, Additive Manufacturing of Mechanically Isotropic Thin Films and Membranes via Microextrusion 3D Printing of Polymer Solutions, ACS Applied Materials & Interfaces 11(6) (2019) 6652-6661.
[48] M.R. Chowdhury, J. Steffes, B.D. Huey, J.R. McCutcheon, 3D printed polyamide membranes for desalination, Science 361(6403) (2018) 682-686.

[49] S. Yuan, D. Strobbe, J.-P. Kruth, P. Van Puyvelde, B. Van der Bruggen, Super-hydrophobic 3D printed polysulfone membranes with a switchable wettability by self-assembled candle soot for efficient gravity-driven oil/water separation, Journal of Materials Chemistry A 5(48) (2017) 25401-25409.
[50] S. Yuan, J. Zhu, Y. Li, Y. Zhao, J. Li, P. Van Puyvelde, B. Van der Bruggen, Structure architecture of micro/nanoscale ZIF-L on a 3D printed membrane for a superhydrophobic and underwater superoleophobic surface, Journal of Materials Chemistry A 7(6) (2019) 2723-2729.
[51] J. Seo, D.I. Kushner, M.A. Hickner, 3D Printing of Micropatterned Anion Exchange Membranes, ACS Applied Materials & Interfaces 8(26) (2016) 16656-16663.
[52] M. Czölderová, M. Behúl, J. Filip, P. Zajíček, R. Grabic, A. Vojs-Staňová, M. Gál, K. Kerekeš, J. Híveš, J. Ryba, M. Rybanská, P. Brandeburová, T. Mackuľak, 3D printed polyvinyl alcohol ferrate(VI) capsules: Effective means for the removal of pharmaceuticals and illicit drugs from wastewater, Chemical Engineering Journal 349 (2018) 269-275.
[53] Y. Dong, S.-Q. Fan, Y. Shen, J.-X. Yang, P. Yan, Y.-P. Chen, J. Li, J.-S. Guo, X.-M. Duan, F. Fang, S.-Y. Liu, A Novel Bio-carrier Fabricated Using 3D Printing Technique for Wastewater Treatment, Scientific Reports 5 (2015) 12400.
[54] O. Elliott, S. Gray, M. McClay, B. Nassief, A. Nunnelley, E. Vogt, J. Ekong, K. Kardel, A. Khoshkhoo, G. Proaño, D.M. Blersch, A.L. Carrano, Design and Manufacturing of High Surface Area 3D-Printed Media for Moving Bed Bioreactors for Wastewater Treatment, Journal of Contemporary Water Research & Education 160(1) (2017) 144-156.
[55] Y. Li, T. Gao, Z. Yang, C. Chen, W. Luo, J. Song, E. Hitz, C. Jia, Y. Zhou, B. Liu, B. Yang, L. Hu, 3D-Printed, All-in-One Evaporator for High-Efficiency Solar Steam Generation under 1 Sun Illumination, Advanced Materials 29(26) (2017) 1700981.
[56] Y. Li, T. Gao, Z. Yang, C. Chen, Y. Kuang, J. Song, C. Jia, E.M. Hitz, B. Yang, L.J.N.E. Hu, Graphene oxide-based evaporator with one-dimensional water transport enabling high-efficiency solar desalination, 41 (2017) 201-209.
[57] P. He, X. Tang, L. Chen, P. Xie, L. He, H. Zhou, D. Zhang, T.J.A.F.M. Fan, Patterned Carbon Nitride–Based Hybrid Aerogel Membranes via 3D Printing for Broadband Solar Wastewater Remediation, 28(29) (2018) 1801121.
[58] Z. Wang, J. Wang, M. Li, K. Sun, C.-j.J.S.r. Liu, Three-dimensional printed acrylonitrile butadiene styrene framework coated with Cu-BTC metal-organic frameworks for the removal of methylene blue, 4 (2014) 5939.
[59] A. Figuerola, D.A. Medina, A.J. Santos-Neto, C.P. Cabello, V. Cerdà, G.T. Palomino, F.J.A.M.T. Maya, Metal–organic framework mixed-matrix coatings on 3D printed devices, 16 (2019) 21-27.
[60] Y. Yang, X. Li, X. Zheng, Z. Chen, Q. Zhou, Y. Chen, 3D-Printed Biomimetic Super-Hydrophobic Structure for Microdroplet Manipulation and Oil/Water Separation, Advanced Materials 30(9) (2018) 1704912.
[61] C. Yan, Z. Ji, S. Ma, X. Wang, F. Zhou, 3D Printing as Feasible Platform for On-Site Building Oil-Skimmer for Oil Collection from Spills, Advanced Materials Interfaces 3(13) (2016) 1600015.
[62] Z. Chen, D. Zhang, E. Peng, J. Ding, 3D-printed ceramic structures with in situ grown whiskers for effective oil/water separation, Chemical Engineering Journal 373 (2019) 1223-1232.
[63] J. Lv, Z. Gong, Z. He, J. Yang, Y. Chen, C. Tang, Y. Liu, M. Fan, W.-M. Lau, 3D printing of a mechanically durable superhydrophobic porous membrane for oil–water separation, Journal of Materials Chemistry A 5(24) (2017) 12435-12444.
[64] A.R. Da Costa, A.G. Fane, D.E. Wiley, Spacer characterization and pressure drop modelling in spacer-filled channels for ultrafiltration, Journal of Membrane Science 87(1) (1994) 79-98.
[65] A.R. Da Costa, A.G. Fane, C.J.D. Fell, A.C.M. Franken, Optimal channel spacer design for ultrafiltration, Journal of Membrane Science 62(3) (1991) 275-291.
[66] W.M. F. Li, A. de Haan, T. Reith, Spacer for use in a membrane separation device and a membrane separation device comprising such a spacer,, World Intellectual Property Organization (2004) WO 2004/112945 A1.
[67] J.R. Werber, C.O. Osuji, M. Elimelech, Materials for next-generation desalination and water purification membranes, Nature Reviews Materials 1 (2016) 16018.

[68] Y. Ying, W. Ying, Q. Li, D. Meng, G. Ren, R. Yan, X. Peng, Recent advances of nanomaterial-based membrane for water purification, Applied Materials Today 7 (2017) 144-158.

[69] Y.C. Woo, Y. Kim, M. Yao, L.D. Tijing, J.-S. Choi, S. Lee, S.-H. Kim, H.K. Shon, Hierarchical composite membranes with robust omniphobic surface using layer-by-layer assembly technique, Environmental science & technology 52(4) (2018) 2186-2196.

[70] M. Yao, J. Ren, N. Akther, Y.C. Woo, L.D. Tijing, S.-H. Kim, H.K. Shon, Improving membrane distillation performance: Morphology optimization of hollow fiber membranes with selected non-solvent in dope solution, Chemosphere 230 (2019) 117-126.

[71] L.D. Tijing, J.-S. Choi, S. Lee, S.-H. Kim, H.K. Shon, Recent progress of membrane distillation using electrospun nanofibrous membrane, Journal of Membrane Science 453 (2014) 435-462.

[72] L.D. Tijing, Y.C. Woo, W.-G. Shim, T. He, J.-S. Choi, S.-H. Kim, H.K. Shon, Superhydrophobic nanofiber membrane containing carbon nanotubes for high-performance direct contact membrane distillation, Journal of Membrane Science 502 (2016) 158-170.

[73] M. Yao, Y.C. Woo, L.D. Tijing, W.-G. Shim, J.-S. Choi, S.-H. Kim, H.K. Shon, Effect of heat-press conditions on electrospun membranes for desalination by direct contact membrane distillation, Desalination 378 (2016) 80-91.

[74] L.D. Tijing, Y.C. Woo, J.-S. Choi, S. Lee, S.-H. Kim, H.K. Shon, Fouling and its control in membrane distillation—A review, Journal of Membrane Science 475 (2015) 215-244.

[75] T. Femmer, A.J.C. Kuehne, M. Wessling, Print your own membrane: direct rapid prototyping of polydimethylsiloxane, Lab on a Chip 14(15) (2014) 2610-2613.

[76] A.N. Sue Mecham, Rima Janusziewicz, Benny D. Freeman and Joseph M. DeSimone, Continuous liquid interface production (CLIP) of precise membrane structures, North American Membrane Society Meeting, Boston, USA, 2015.

[77] W. Lin, Enhanced continuous liquid interface production with track-etched membrane, Rapid Prototyping Journal 25(1) (2019) 117-125.

[78] L. Hernandez-Afonso, R. Fernandez-Gonzalez, P. Esparza, M.E. Borges, S. Diaz Gonzalez, J. Canales-Vasquez, J.C. Ruiz-Morales, Ceramic-Based 3D Printed Supports for Photocatalytic Treatment of Wastewater, Journal of Chemistry 2017 (2017) 9.

[79] A. Kudo, Y.J.C.S.R. Miseki, Heterogeneous photocatalyst materials for water splitting, 38(1) (2009) 253-278.

[80] A. Vyatskikh, A. Kudo, S. Delalande, J.R.J.M.T.C. Greer, Additive manufacturing of polymer-derived titania for one-step solar water purification, 15 (2018) 288-293.

[81] A. Sangiorgi, Z. Gonzalez, A. Ferrandez-Montero, J. Yus, A. Sanchez-Herencia, C. Galassi, A. Sanson, B.J.J.o.T.E.S. Ferrari, 3D Printing of Photocatalytic Filters Using a Biopolymer to Immobilize TiO2 Nanoparticles, 166(5) (2019) H3239-H3248.

[82] M.J.M. de Vidales, A. Nieto-Márquez, D. Morcuende, E. Atanes, F. Blaya, E. Soriano, F.J.C.T. Fernández-Martínez, 3D printed floating photocatalysts for wastewater treatment, (2019).

[83] A. Vyatskikh, A. Kudo, S. Delalande, J.R. Greer, Additive manufacturing of polymer-derived titania for one-step solar water purification, Materials Today Communications 15 (2018) 288-293.

[84] Y. de Rancourt de Mimérand, K. Li, J. Guo, Photoactive Hybrid Materials with Fractal Designs Produced via 3D Printing and Plasma Grafting Technologies, ACS Applied Materials & Interfaces 11(27) (2019) 24771-24781.

[85] X. Zhou, C.-j. Liu, Three-dimensional Printing for Catalytic Applications: Current Status and Perspectives, Advanced Functional Materials 27(30) (2017) 1701134.

[86] Prabhat K. Rai, J. Lee, S.K. Kailasa, E.E. Kwon, Y.F. Tsang, Y.S. Ok, K.-H. Kim, A critical review of ferrate(VI)-based remediation of soil and groundwater, Environmental Research 160 (2018) 420-448.

[87] B. Yuan, Y. Chen, M.-L. Fu, Degradation efficiencies and mechanisms of trichloroethylene (TCE) by controlled-release permanganate (CRP) oxidation, Chemical Engineering Journal 192 (2012) 276-283.

[88] K. Biswas, Taylor, M.W. & Turner, S.J., Successional development of biofilms in moving bed biofilm reactor (MBBR) systems treating municipal wastewater, Appl Microbiol Biotechnol 98 (2014) 1429.

[89] B. Tang, Y. Zhao, L. Bin, S. Huang, F. Fu, Variation of the characteristics of biofilm on the semi-suspended bio-carrier produced by a 3D printing technique: Investigation of a whole growing cycle, Bioresource Technology 244 (2017) 40-47.

[90] B. Tang, H. Song, L. Bin, S. Huang, W. Zhang, F. Fu, Y. Zhao, Q. Chen, Determination of the profile of DO and its mass transferring coefficient in a biofilm reactor packed with semi-suspended bio-carriers, Bioresource Technology 241 (2017) 54-62.
[91] Z. Jiang, L.D. Tijing, A. Amarjargal, C.H. Park, K.-J. An, H.K. Shon, C.S. Kim, Removal of oil from water using magnetic bicomponent composite nanofibers fabricated by electrospinning, Composites Part B: Engineering 77 (2015) 311-318.
[92] J.H. Shin, J.-H. Heo, S. Jeon, J.H. Park, S. Kim, H.-W. Kang, Bio-inspired hollow PDMS sponge for enhanced oil–water separation, Journal of Hazardous Materials 365 (2019) 494-501.
[93] R. Xing, B. Yang, R. Huang, W. Qi, R. Su, B.P. Binks, Z. He, Three-Dimensionally Printed Bioinspired Superhydrophobic Packings for Oil-in-Water Emulsion Separation, Langmuir 35(39) (2019) 12799-12806.
[94] P.J.E.S.N. Wang, Emerging investigator series: the rise of nano-enabled photothermal materials for water evaporation and clean water production by sunlight, 5(5) (2018) 1078-1089.
[95] Y.-S. Jun, X. Wu, D. Ghim, Q. Jiang, S. Cao, S.J.A.o.c.r. Singamaneni, Photothermal Membrane Water Treatment for Two Worlds, (2019).
[96] Y. Li, T. Gao, Z. Yang, C. Chen, W. Luo, J. Song, E. Hitz, C. Jia, Y. Zhou, B.J.A.M. Liu, 3D-printed, all-in-one evaporator for high-efficiency solar steam generation under 1 sun illumination, 29(26) (2017) 1700981.
[97] Y. Li, T. Gao, Z. Yang, C. Chen, Y. Kuang, J. Song, C. Jia, E.M. Hitz, B. Yang, L. Hu, Graphene oxide-based evaporator with one-dimensional water transport enabling high-efficiency solar desalination, Nano Energy 41 (2017) 201-209.
[98] K. Fu, Y. Yao, J. Dai, L.J.A.M. Hu, Progress in 3D printing of carbon materials for energy-related applications, 29(9) (2017) 1603486.
[99] E.B. Secor, M.C. Hersam, Emerging Carbon and Post-Carbon Nanomaterial Inks for Printed Electronics, The Journal of Physical Chemistry Letters 6(4) (2015) 620-626.
[100] F. Torrisi, T. Hasan, W. Wu, Z. Sun, A. Lombardo, T.S. Kulmala, G.-W. Hsieh, S. Jung, F. Bonaccorso, P.J. Paul, D. Chu, A.C. Ferrari, Inkjet-Printed Graphene Electronics, ACS Nano 6(4) (2012) 2992-3006.
[101] A. Kamyshny, S. Magdassi, Conductive Nanomaterials for Printed Electronics, 10(17) (2014) 3515-3535.
[102] P. Zhang, Q. Liao, H. Yao, H. Cheng, Y. Huang, C. Yang, L. Jiang, L. Qu, Three-dimensional water evaporation on a macroporous vertically aligned graphene pillar array under one sun, Journal of Materials Chemistry A 6(31) (2018) 15303-15309.
[103] Z. Liu, X. Zhou, C.-j.J.D. Liu, R. Materials, N-doped porous carbon material prepared via direct ink writing for the removal of methylene blue, 95 (2019) 121-126.
[104] Y. Wang, X. Ling, Y. Wang, J.J.D. Zhang, R. Materials, Probing the effect of doped F and N on the structures and properties of fullerene-like hydrogenated carbon films, 79 (2017) 32-37.
[105] A.D. Valino, J.R.C. Dizon, A.H. Espera, Q. Chen, J. Messman, R.C. Advincula, Advances in 3D printing of thermoplastic polymer composites and nanocomposites, Progress in Polymer Science 98 (2019) 101162.
[106] D. Zhang, J. Xiao, Q. Guo, J.J.J.o.M.S. Yang, 3D-printed highly porous and reusable chitosan monoliths for Cu(II) removal, 54(8) (2019) 6728-6741.
[107] Y. Hu, X. Liu, J. Bai, K. Shih, E.Y. Zeng, H.J.E.S. Cheng, P. Research, Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization, 20(9) (2013) 6150-6159.
[108] D. Zhang, J. Xiao, Q. Guo, J.J.J.o.M.S. Yang, 3D-printed highly porous and reusable chitosan monoliths for Cu (II) removal, 54(8) (2019) 6728-6741.
[109] G.A. Appuhamillage, D.R. Berry, C.E. Benjamin, M.A. Luzuriaga, J.C. Reagan, J.J. Gassensmith, R.A. Smaldone, A biopolymer-based 3D printable hydrogel for toxic metal adsorption from water, Polymer International 68(5) (2019) 964-971.
[110] P. Sun, L. Zhang, S. Tao, Preparation of hybrid chitosan membranes by selective laser sintering for adsorption and catalysis, Materials & Design 173 (2019) 107780.
[111] F. Niesler, M. Hermatschweiler, Two-Photon Polymerization — A Versatile Microfabrication Tool, Laser Technik Journal 12(3) (2015) 44-47.

[112] J.R.C. Dizon, Q. Chen, A.D. Valino, R.C. Advincula, Thermo-mechanical and swelling properties of three-dimensional-printed poly (ethylene glycol) diacrylate/silica nanocomposites, MRS Communications 9(1) (2019) 209-217.
[113] J.R. Tumbleston, D. Shirvanyants, N. Ermoshkin, R. Janusziewicz, A.R. Johnson, D. Kelly, K. Chen, R. Pinschmidt, J.P. Rolland, A. Ermoshkin, E.T. Samulski, J.M. DeSimone, Continuous liquid interface production of 3D objects, Science 347(6228) (2015) 1349-1352.
[114] A.J. Scardino, H. Zhang, D.J. Cookson, R.N. Lamb, R.d. Nys, The role of nano-roughness in antifouling, Biofouling 25(8) (2009) 757-767.
[115] P. Azimi, D. Zhao, C. Pouzet, N.E. Crain, B. Stephens, Emissions of Ultrafine Particles and Volatile Organic Compounds from Commercially Available Desktop Three-Dimensional Printers with Multiple Filaments, Environmental Science & Technology 50(3) (2016) 1260-1268.
[116] Y. Kim, C. Yoon, S. Ham, J. Park, S. Kim, O. Kwon, P.-J. Tsai, Emissions of Nanoparticles and Gaseous Material from 3D Printer Operation, Environmental Science & Technology 49(20) (2015) 12044-12053.
[117] P. Graff, B. Ståhlbom, E. Nordenberg, A. Graichen, P. Johansson, H. Karlsson, Evaluating Measuring Techniques for Occupational Exposure during Additive Manufacturing of Metals: A Pilot Study, Journal of Industrial Ecology 21(S1) (2017) S120-S129.
[118] D.R. I. Gibson, and B. Stucker, Additive manufacturing technologies: 3D printing, rapid prototyping, and direct digital manufacturing (2nd ed), Springer2014.
[119] J. Faludi, Comparing environmental impacts of additive manufacturing vs traditional machining via life-cycle assessment, Rapid Prototyping Journal 21(1) (2015) 14-33.
[120] R. LaSelle, Five critical shifts guiding the future of 3D printing, Retieved from https://www.jabil.com/insights/blog-main/future-of-3d-printing-additive-manufacturing-looks-bright.html (2019).
[121] S.A.M. Tofail, E.P. Koumoulos, A. Bandyopadhyay, S. Bose, L. O'Donoghue, C. Charitidis, Additive manufacturing: scientific and technological challenges, market uptake and opportunities, Materials Today 21(1) (2018) 22-37.
[122] L. Greguric, Can 3D printing be used for mass production?, Retrived from https://all3dp.com/2/can-3d-printing-be-used-for-mass-production/ (2019).
[123] C. Schmidt, The future of additive manufacturing, Retrieved from https://medium.com/@christina_39925/the-future-of-additive-manufacturing-6396d191183e (2018).
[124] S.J. Lee, D.N. Heo, J.S. Park, S.K. Kwon, J.H. Lee, J.H. Lee, W.D. Kim, I.K. Kwon, S.A. Park, Characterization and preparation of bio-tubular scaffolds for fabricating artificial vascular grafts by combining electrospinning and a 3D printing system, Physical Chemistry Chemical Physics 17(5) (2015) 2996-2999.
[125] I. Rajzer, A. Kurowska, A. Jabłoński, S. Jatteau, M. Śliwka, M. Ziąbka, E. Menaszek, Layered gelatin/PLLA scaffolds fabricated by electrospinning and 3D printing- for nasal cartilages and subchondral bone reconstruction, Materials & Design 155 (2018) 297-306.
[126] S. Naghieh, E. Foroozmehr, M. Badrossamay, M. Kharaziha, Combinational processing of 3D printing and electrospinning of hierarchical poly(lactic acid)/gelatin-forsterite scaffolds as a biocomposite: Mechanical and biological assessment, Materials & Design 133 (2017) 128-135.
[127] J.R.C. Dizon, Valino, A.D., Souza, L.R., Espera Jr., A.H., Chen, Q,, Advincula, R.C. , 3D-Printed Molds and Materials for Injection Molding and Rapid Tooling Applications, MRS Communications (2019 (Just accepted)).
[128] Large 3D printer ready to build, Metal Powder Report 74(3) (2019) 163-164.
[129] F. Momeni, S. M.Mehdi Hassani.N, X. Liu, J. Ni, A review of 4D printing, Materials & Design 122 (2017) 42-79.
[130] J. Zhou, S.S. Sheiko, Reversible shape-shifting in polymeric materials, Journal of Polymer Science Part B: Polymer Physics 54(14) (2016) 1365-1380.
[131] S. Tibbits, 4D Printing: Multi-Material Shape Change, Architectural Design 84(1) (2014) 116-121.
[132] D. Raviv, W. Zhao, C. McKnelly, A. Papadopoulou, A. Kadambi, B. Shi, S. Hirsch, D. Dikovsky, M. Zyracki, C. Olguin, R. Raskar, S. Tibbits, Active Printed Materials for Complex Self-Evolving Deformations, Scientific Reports 4 (2014) 7422.

[133] M. Vaezi, S. Chianrabutra, B. Mellor, S. Yang, Multiple material additive manufacturing – Part 1: a review, Virtual and Physical Prototyping 8(1) (2013) 19-50.
[134] Q. Ge, H.J. Qi, M.L. Dunn, Active materials by four-dimension printing, Applied Physics Letters 103(13) (2013) 131901.
[135] Q. Zhang, K. Zhang, G. Hu, Smart three-dimensional lightweight structure triggered from a thin composite sheet via 3D printing technique, Scientific Reports 6 (2016) 22431.
[136] A. Sydney Gladman, E.A. Matsumoto, R.G. Nuzzo, L. Mahadevan, J.A. Lewis, Biomimetic 4D printing, Nature Materials 15 (2016) 413.
[137] O. Kuksenok, A.C. Balazs, Stimuli-responsive behavior of composites integrating thermo-responsive gels with photo-responsive fibers, Materials Horizons 3(1) (2016) 53-62.
[138] G. Villar, A.D. Graham, H. Bayley, A Tissue-Like Printed Material, Science 340(6128) (2013) 48-52.
[139] D. Kokkinis, M. Schaffner, A.R. Studart, Multimaterial magnetically assisted 3D printing of composite materials, Nature Communications 6 (2015) 8643.
[140] M. Nadgorny, Z. Xiao, C. Chen, L.A. Connal, Three-Dimensional Printing of pH-Responsive and Functional Polymers on an Affordable Desktop Printer, ACS Applied Materials & Interfaces 8(42) (2016) 28946-28954.
[141] A.S. Mathews, S. Abraham, S.K. Kumaran, J. Fan, C. Montemagno, Bio nano ink for 4D printing membrane proteins, RSC Advances 7(66) (2017) 41429-41434.
[142] S. Miao, N. Castro, M. Nowicki, L. Xia, H. Cui, X. Zhou, W. Zhu, S.-j. Lee, K. Sarkar, G. Vozzi, Y. Tabata, J. Fisher, L.G. Zhang, 4D printing of polymeric materials for tissue and organ regeneration, Materials Today 20(10) (2017) 577-591.