3D-Printing of porous materials: Application to Metal-Organic Frameworks

David Pianca, Michaël Carboni, Daniel Meyer

3D-Printing of porous materials: Application to Metal-Organic Frameworks

David PIANCA[a], Michaël CARBONI[a*], Daniel MEYER[a]

[a] *ICSM, Univ Montpellier, CEA, CNRS, ENSCM, Marcoule, France*

Abstract

MOFs (Metal-Organic Frameworks) are crystalline porous organic/inorganic hybrid materials with well-defined structures that have proven to possess a great potential in many applications, mostly because during the synthesis of these materials the structure can be controlled to add the desired functionality in either the metal cluster or the linker. Unfortunately, few methods are reported to shape these materials as manipulable and, most importantly, to retain their original properties. Recently, 3D printing of MOF has been proposed and shows promising properties to obtain an object, which can be designed upon request. We propose here to summarize the main development of 3D printing of MOF to determine some prospects and opportunities in this area.

Keywords: Metal-Organic Frameworks; 3D-printing; Shaping

Corresponding information:

* michael.carboni@cea.fr / tel: (+33) 466 339 204 / ICSM, UMR 5257, Bât 426, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France

Introduction

Porous materials (carbon, silica or even coordination polymers (including MOF, Metal-Organic Frameworks)) have attracted a lot of attention in recent years because of their tremendous properties for many applications. Unfortunately, the literature currently lacks simple and economical manufacturing processes for porous materials that do not alter their properties (mostly porosity). However, many applications of MOFs require mastering the shaping of the material in order to implement it industrially. Although relatively few studies have been published to date, the field is expanding fast in terms of techniques and understanding of the stability of MOFs and its accessibility in hierarchically porous materials rather than powders.[1]

A number of procedures used to fix powders onto a support have been successfully applied to MOFs. The simplest involves the compaction of pre-synthesized MOFs, a well-established method in the pharmaceutical and agrochemical industries. Unfortunately, the compaction process considerably reduces the porosity of the powders and is not suitable for the formation of macropores in the final material. They can also be shaped into more robust materials through pressure, granulation, extrusion, spray drying and even 3D printing. MOFs can also be deposited as thin films on various substrates by layer-by-layer assembly, spin coating, and electrochemical deposition mainly for application as photosynthetic device or as an electrode.[2] Among all these approaches, 3D printing allows to directly create complex structural networks with much less waste than with other techniques. This technique gives access to the formation of complex 3D structures giving initially a fast access to prototyping and then to lay the basis for an industrial development. More specifically such approaches look promising in shaping the functional porous powder as solid.

The printing of MOFs is possible by using the direct ink writing (DIW) technology were MOFs are mixed with a “paste” to form an ink that is directly deposited on the hotbed of the printer to solidify. This simple method presents a low resolution in terms of end product obtained with a size limitation because the past must be close to the warm bed. Another promising way is to use fuse filament or SLA (Stereolithography) techniques, where MOFs are directly incorporated in a composite filament or resin that is directly used to print with common 3D-printers. The main advantages of such way is to keep the resolution of the original printer. These ways are very promising because there will be no more limitations of size or resolution, but the challenge is to let the powder accessible as much as possible to keep the porous properties of the final object. Finally, MOFs can also be deposited to a support that is obtained by 3D printing. Solely few papers are reporting the use of 3D printing to shape MOFs as a solid material. This review provides a brief summary of MOF's latest 3D printing achievements and some perspectives and opportunities in this area.

Direct ink

With this technique an ink, containing the MOFs is directly deposited on the bed of the printer leading to the solidification of the ink. Additive preparations are usually composed of solvents, thermoset polymers and adhesive polymers. Such formulation is close to those that our group has proposed to form monoliths by Pickering emulsion[3,4] and need a research effort to optimize and characterize the viscosity and other rheological properties of the ink to optimize the deposition.

Thakkar *et al.*[5] were able to shape MOF-74 (Ni) and UTSA-16(Co) with this methodology. The formulation of the ink, typically for the Ni-MOF, is composed of bentonite clay (15 %), PVA (PolyVinyl alcohol, 5 %), MOFs (80 %) dispersed in deionized water and ethanol (5:95) (**Figure 1**). The dough was then loaded into a syringe and extruded from a 0.85 mm diameter nozzle by pressing (2–5 psig) air into the syringe to print monoliths. The nitrogen sorption's show type I isotherm[6] for the powders as well the monoliths with a loss of the specific area (from 1180 and 727 $m^2.g^{-1}$ to 737 and 568 $m^2.g^{-1}$ as monoliths respectively fort MOF-74 and UTSA-16). Both materials have CO_2 sorption ability and experiments showed that, upon exposure to 5000 ppm CO_2 at 25 °C, the MOF74(Ni) and UTSA-16(Co) monoliths can adsorb CO_2 with uptake capacities which are 79% and 87% of the capacities of their MOF analogues respectively under the same conditions.

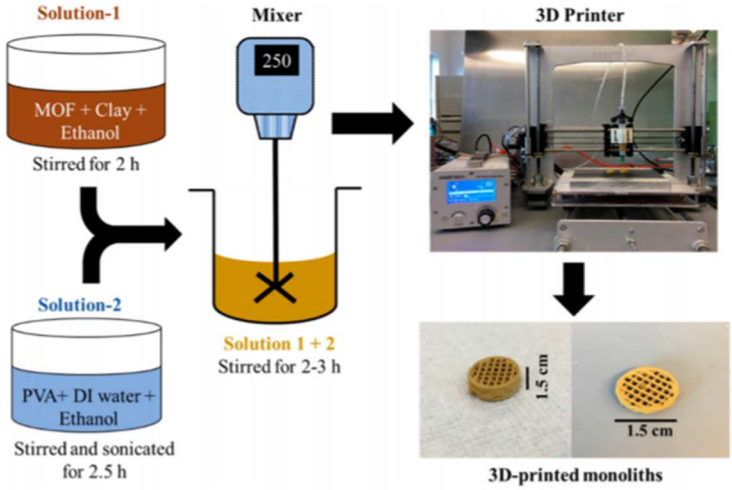

Figure 1 Schematic of the 3D-printed MOF monolith preparation procedure. Reprinted with permission from [5]. Copyright 2017 American Chemical Society.

Dhainaut *et al.*[7] target to shape HKUST-1 (Cu), CPL-1 (Cu), ZIF-8 (Zn), and UiO-66-NH_2 (Zr) with an approach that also employs modified 3D printers that extrude inks formulated in the presence of an organic binder. The ink, typically for HKUST-1, was composed of 0.25 % MOF, 0.01% PVA, 0.02 % of HEC (Hexylethylcellulose) and 0.65% of mixture composed of 50 % vol. of water and 50 % vol. of ethanol [7]. After shaping, the object containing HKUST-1 presents a specific area of 1188$m^2.g^{-1}$ (1466 $m^2.g^{-1}$ for the original powder) and so a loss of approximately 20 % of the

original surface area. According to the authors, this loss is due to the partial degradation of MOF when printed with a polar solvent. Ink formulation with MOF is crucial for controlling physical properties (such as shear-thinning) for the ultimate porosity of the object. The authors state that for methane storage application (HKUST-1, ZIF-8, and UiO66-NH_2) or for ethane/ethylene separation (CPL-1), the 3D printed solids displayed performances which are in accordance with the literature. Evaluation of the mechanical properties (**Figure 2**) has revealed that one to two orders of magnitude of compressive strength difference can be observed between the 3D-printed samples compared to analogous binderless tablets. This work exhibits the importance of the right formulation to have a good balance between mechanical stability of the materials and the persist of the porosity of the 3D-printed solid.

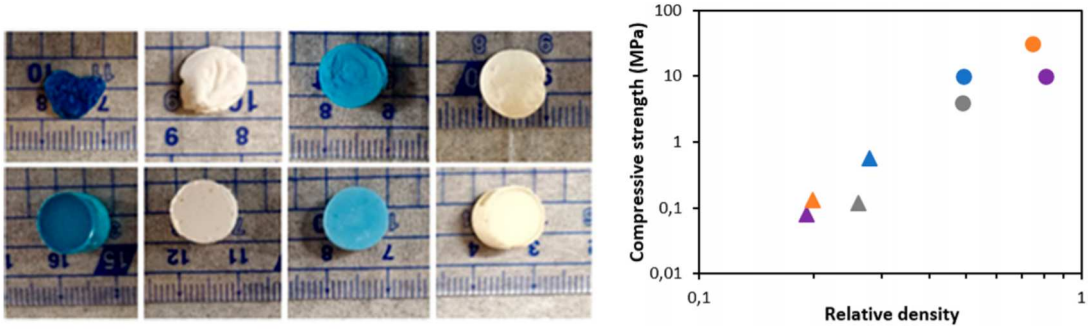

Figure 2 Left : 3D-printed solids (top) andtheir binderless, pelletized counterparts (bottom). Right: Compressive strength as a function of the relative density of 3D-printed solids (▲) and binderless pellets (●) of CPL-1 (blue), HKUST-1 (purple), ZIF-8 (gray), and UiO-66-NH_2 (orange). Reprinted with permission from [7]. Copyright 2020 American Chemical Society.

Young *et al.* have reported DIW strategy of 3D printing of UiO-66 (Zr). [8] The proposed method is slightly different as they used a 365 nm light source upon extrusion to have a UV-crosslinking of a photo-initiator and allow the shape retention. The ink contains UiO-66 particles (52 %), a polymer binding agent (44 %) and a photoinitiator (4 %). After printing, the object exhibits no porosity then it was activated (thermal degradation of the polymer binder, 280 °C) to recover some porosity properties of UiO-66. The specific area obtained is 633 $m^2.g^{-1}$. The loss of specific area is approximately of 60% (original UiO-66 exhibits a surface area of 1590 $m^2.g^{-1}$).

Lawson *et al.* [9], have proposed a 2-fold approach to formulate polymer-MOFs (MOF-74 (Ni) and HKUST-1) monoliths and provides a pathway of overcoming the solvent expulsion and particle agglomeration (this effect was observed with bentonite[10]). The ink is made up of MOF, Torlon (a polyamide-imide, 4000 T), PVP (poly-(vinylpyrrolidone)), NMP (N-methyl-2-pyrrolidone), DMF and water. Only HKUST-1 retained its crystallinity (microporous structure) and MOF-74 broke down. However, although decomposition was noted for MOF-74, the release of the ligands and metals is used as seeds for a secondary growth. The results of this study demonstrate that the direct printing of precursor seeds followed by secondary growth is an appropriate approach to the formulation of

polymeric monoliths-MOF. In another work, Lawson *et al*. [10] propose a printable sol–gel HKUST-1 precursors (70 weight %) and optimized the in situ growth conditions by varying the desolvation temperature and activation solvent. Schematic representation of the synthetic approach is presented in **Figure 3**. The originality of this work was to print the precursors of the MOFs instead of directly the MOFs to obtain an ink with favorable rheological properties for the 3D printing. After printing the synthetic sol-gel, MOF can be easily synthesized in situ by applying heat, eliminating solvents and activating solvents. This strategy is also compared with the direct printing of HKUST-1. HKUST-1 monolith obtained by this gel-process-growth technique has comparable adsorption capacity and adsorbent loading to that monolith printed directly with the MOF, but with an enhancement of the mass transfer kinetics during the printing by addressing the rheological shortcomings of MOF DIW.

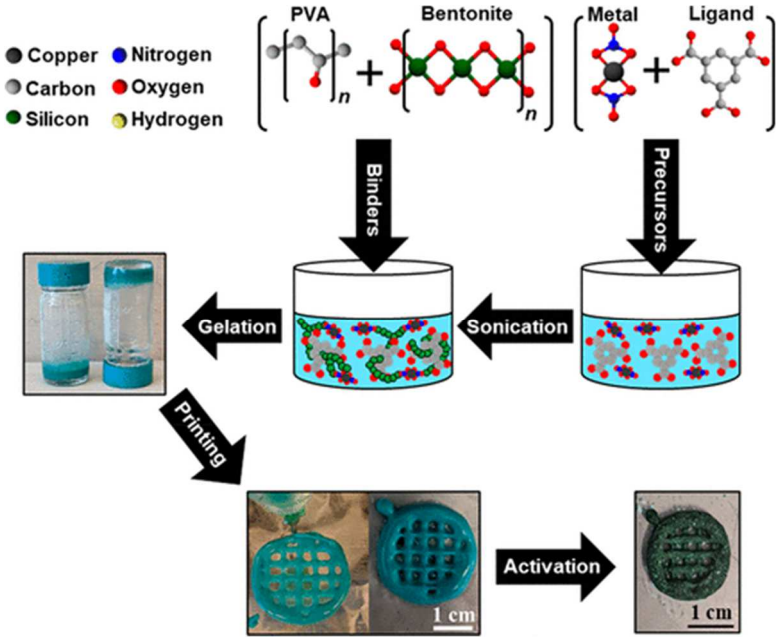

Figure 3 Schematic representation of the proposed gel-print-grow technique. Reprinted with permission from [10]. Copyright 2020 American Chemical Society.

Pei *et al*. have also reported the 3D-printing of HKUST-1 with biocompatible polymers and the use of sodium alginate and gelatin, in water, as matrix to shape MOFs as tools for the removal of organic pollutants.[11] Finally, by adjusting the parameters, the object could have an adsorption efficiency of 99.8% at 20 minutes under its study conditions. More importantly, their 3D-printed adsorbents can be easily regenerated in dilute acid solution and reused for at least 7 times without performance loss whereas experiments with MOF powder is not allowing more than 2 regeneration of the materials.

In summary, the DIW is a simple method to shape MOF with 3D printer but it needs a specific and costly printer or, in majority of published works, the modification of a fused filaments 3D printer decreasing drastically the precision and the size of the printed object. With the DIW technique, the ink

need to solidify quite quickly to increase the size of the object and in majority of cases it need some heat from on hot bed limiting the possibility to have a big object. However, the rheological properties of the ink are the masterpiece and more research need to be done in this field to find the best composition that shape MOFs into an object that keep original properties of the powder and have a good compressive strength.

Indirect 3D printing

Another simple solution for getting an object containing MOF is to add the active materials to a medium that has been 3D printed. The advantages of such a method are to preserve the original properties of the MOFs and to allow the accessibility of the particles to the surface of the object.

A method was developed to produce HKUST-1 on an acrylonitrile butadiene styrene (ABS) skeleton.[12] This method is based on various treatments that enable in-situ step-by-step growth of the MOF directly on an ABS filter. To realize these steps the authors prepare two solutions containing the ligand and triethylamine (solution A) and an another composed by the metal precursor $Cu(NO_3)_2$ (solution B) (**Figure 4**). The skeleton is then immersed during 4 hours in the solution A and then 4 hours in the solution B. This cycle was repeated for 1 to 8 times to create a multilayer of MOFs. The 3D-printed filter is then successfully used for dye adsorption and show the removal of 93.3% and 98.3% (for a dye concentration in solution of 10 and 5 mg/L respectively) within 10 min. The Cu-BTC/ABS composites can be reused (up to 5 cycles) and the ABS polymer skeleton can be recovered and reused for secondary Cu-BTC growth.

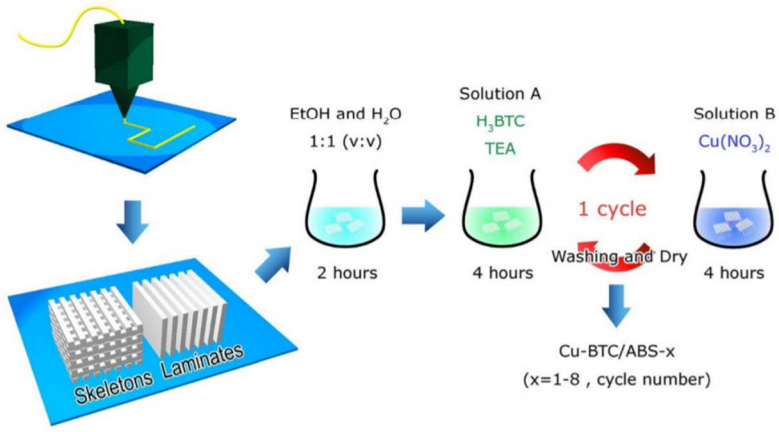

Figure 4 Fabrication of Cu-BTC/ABS composites. Reprinted with permission from [12]

Another strategy has been proposed with the deposition of ZIF-67 directly on a 3D-printed object printed by a SLA (Stereolithography technology) printer and the use of a clear photoactive resin composed of methacrylate. [13] SLA uses a photopolymer resin sensitive to ultraviolet light that will be photo chemically solidified after excitation at a specific wavelength. A formulation is proposed via

the dispersion of MOFs in polyvinylidene fluoride/dimethylformamide (PVDF/DMF) mixtures to obtain a MOF-mixed-matrix that can be coated onto a 3D-printed object after a drying step (nitrogen flow) and a heating process at 60°C in an oven.

Lastly, it was proposed by Pellejero *et al.*[14] the formation of a ZIF-8 on ABS filament. To prepare this filament, the synthesis strategy consists in low temperature ALD (Atomic Layer Deposition) of ZnO on the ABS grid followed by the hydrothermal conversion of ZnO to ZIF-8 on the ABS support. The ABS/ZIF-8 filters have adsorption behavior for dimethylmethylphosphonate and demonstrate potential applications for capturing toxic gases.

Even if these examples seem easy to set up, the main disadvantages of such technique is probably to fix the MOFs on the surface that stay on the support after any application.

Fused filaments

Fused filament technology is used most often for 3D printing. The consumable is a plastic filament (primarily PLA, PETG, PCL, ABS …) which is melted into an extruder and drawn on a bed. A composite filament containing the plastic and the MOFs should be design in order to have an homogeneity in the composition of the filament and to keep the accessibility of the MOF in the final structure (after melting the filament and the construction of the object).

The production of MOF–thermoplastic polymer composites has been recently proposed and the impact of filament formulation on porosity access has been studied.[15] Two different filaments were proposed using PLA (rigid) and thermoplastic polyurethane (TPU, semiflex) with a charge of MOF (ZIF-8) up to a mass of 50%.

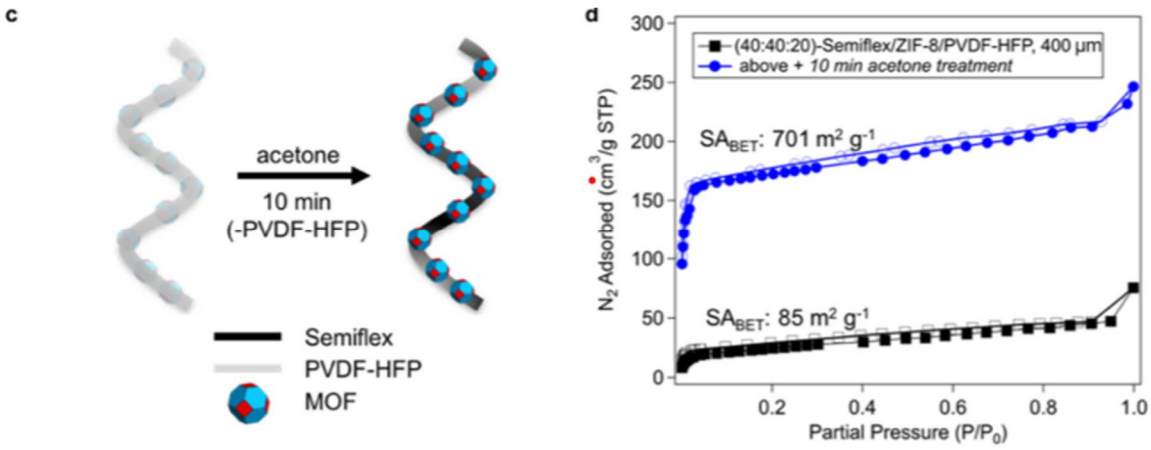

Figure 5 N_2 adsorption/desorption isotherms of Semiflex/ZIF-8/PVDF-HFP 400 µm strands as printed and after acetone treatment. Reprinted with permission from [15]. Copyright 2020 American Chemical Society.

The extruded filament composed of PLA/ZIF-8 exhibits a specific area is 5 $m^2.g^{-1}$ that increase to 141 $m^2.g^{-1}$ with the use of a filament with lower diameter (0.4 mm instead of 1.75 mm). However, a treatment with methanol released the porosity, and the microporosity of ZIF-8 appear and give a specific area of 570 $m^2.g^{-1}$ showing a loss of 67 % of the surface compared with those of ZIF-8 (1750 $m^2.g^{-1}$). The same strategy has been developed with the PLU filament (semiflex) where an aceton treatment is necessary to release the porosity around 700 $m^2.g^{-1}$ with an isotherm of type I as expected for such material (**Figure 5**) [16].

ABS-MOF composite has also been proposed with MOF-5 (Zn based MOF) concentration of 10 % [17]. MOFs and ABS were suspended by sonication, in acetone, to dissolve the ABS and then the mixture is placed on a hot plate to evaporate the solvent and form a film. After this stage, the solution is placed on hot plate to form a film. The film is then cutted and extruded to form a filament that can be directly used in a 3D-printer. MOF-5 was susceptible to moisture and degradation was observed in the incorporation process.

Even if different strategies have been proposed, as shown by the previous examples, the incorporation of MOFs directly in the matrix of a composite is an elegant way to shape porous materials easily, without limitation of size (except the specification of the 3D-printer) and bring to this challenge a new way to shape MOF with high flexibility of structures.

Conclusion

To summarize, different techniques are proposed to shape MOF by 3D-printer but the field is at an early stage of development and only few tries are currently available. The simplest way is

through the direct-ink technology where the MOF is mixed with other chemicals to form a paste that is directly printed. With this technique, the formulation is important to handle between the accessibility of the MOFs to stay porous in the final matrix and the hardness of the object. Moreover, the size will be limited by the possibility of the ink to quickly be solid. Another possibility is the indirect 3D printing with the deposition of MOFs on a pre-print object offering a two-step method to shape the final object. Lastly, the design of a composite filament with MOF seems the most promising direction because this composite can be used directly in a common 3D-printer without limitation of size of the final object and allowing to keep the initial resolution of the printer. Unfortunately, this is also the most challenging way because the accessibility of the MOFs in the final object is the most limited. There are still many difficulties in shaping MOF powder as a solid material, but 3D printing of MOF seems a promising way to achieve this important challenge.

References

[1] F. Lorignon, A. Gossard, M. Carboni, Hierarchically porous monolithic MOFs: An ongoing challenge for industrial-scale effluent treatment, Chem. Eng. J. 393 (2020) 124765. https://doi.org/10.1016/j.cej.2020.124765.
[2] G. Genesio, J. Maynadié, M. Carboni, D. Meyer, Recent status on MOF thin films on transparent conductive oxides substrates (ITO or FTO), New J. Chem. 42 (2018) 2351–2363. https://doi.org/10.1039/C7NJ03171H.
[3] F. Lorignon, A. Gossard, M. Carboni, D. Meyer, Microstructural and rheological investigation of upcycled metal-organic frameworks stabilized Pickering emulsions, J. Colloid Interface Sci. 586 (2021) 305–314. https://doi.org/10.1016/j.jcis.2020.10.093.
[4] F. Lorignon, A. Gossard, M. Carboni, D. Meyer, From wastes to interconnected porous monolith: Upcycling of Al-based metal organic framework via pickering emulsion template, Mater. Lett. 296 (2021) 129931. https://doi.org/10.1016/j.matlet.2021.129931.
[5] H. Thakkar, S. Eastman, Q. Al-Naddaf, A.A. Rownaghi, F. Rezaei, 3D-Printed Metal–Organic Framework Monoliths for Gas Adsorption Processes, ACS Appl. Mater. Interfaces. 9 (2017) 35908–35916. https://doi.org/10.1021/acsami.7b11626.
[6] S. Caspe, The adsorption isotherm?, J. Chem. Educ. 9 (1932) 907. https://doi.org/10.1021/ed009p907.
[7] J. Dhainaut, M. Bonneau, R. Ueoka, K. Kanamori, S. Furukawa, Formulation of Metal–Organic Framework Inks for the 3D Printing of Robust Microporous Solids toward High-Pressure Gas Storage and Separation, ACS Appl. Mater. Interfaces. 12 (2020) 10983–10992. https://doi.org/10.1021/acsami.9b22257.
[8] A.J. Young, R. Guillet-Nicolas, E.S. Marshall, F. Kleitz, A.J. Goodhand, L.B.L. Glanville, M.R. Reithofer, J.M. Chin, Direct ink writing of catalytically active UiO-66 polymer composites, Chem. Commun. 55 (2019) 2190–2193. https://doi.org/10.1039/C8CC10018G.
[9] S. Lawson, M. Snarzyk, D. Hanify, A.A. Rownaghi, F. Rezaei, Development of 3D-Printed Polymer-MOF Monoliths for CO_2 Adsorption, Ind. Eng. Chem. Res. 59 (2020) 7151–7160. https://doi.org/10.1021/acs.iecr.9b05445.
[10] S. Lawson, A.-A. Alwakwak, A.A. Rownaghi, F. Rezaei, Gel–Print–Grow: A New Way of 3D Printing Metal–Organic Frameworks, ACS Appl. Mater. Interfaces. 12 (2020) 56108–56117. https://doi.org/10.1021/acsami.0c18720.
[11] R. Pei, L. Fan, F. Zhao, J. Xiao, Y. Yang, A. Lai, S.-F. Zhou, G. Zhan, 3D-Printed metal-organic frameworks within biocompatible polymers as excellent adsorbents for organic dyes removal, J. Hazard. Mater. 384 (2020) 121418. https://doi.org/10.1016/j.jhazmat.2019.121418.
[12] Z. Wang, J. Wang, M. Li, K. Sun, C. Liu, Three-dimensional Printed Acrylonitrile Butadiene Styrene Framework Coated with Cu-BTC Metal-organic Frameworks for the Removal of Methylene Blue, Sci. Rep. 4 (2015) 5939. https://doi.org/10.1038/srep05939.
[13] A. Figuerola, D.A.V. Medina, A.J. Santos-Neto, C.P. Cabello, V. Cerdà, G.T. Palomino, F. Maya, Metal–organic framework mixed-matrix coatings on 3D printed devices, Appl. Mater. Today. 16 (2019) 21–27. https://doi.org/10.1016/j.apmt.2019.04.011.
[14] I. Pellejero, F. Almazán, M. Lafuente, M.A. Urbiztondo, M. Drobek, M. Bechelany, A. Julbe, L.M. Gandía, Functionalization of 3D printed ABS filters with MOF for toxic gas removal, J. Ind. Eng. Chem. 89 (2020) 194–203. https://doi.org/10.1016/j.jiec.2020.05.013.
[15] K.A. Evans, Z.C. Kennedy, B.W. Arey, J.F. Christ, H.T. Schaef, S.K. Nune, R.L. Erikson, Chemically Active, Porous 3D-Printed Thermoplastic Composites, ACS Appl. Mater. Interfaces. 10 (2018) 15112–15121. https://doi.org/10.1021/acsami.7b17565.
[16] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure Appl. Chem. 87 (2015) 1051–1069. https://doi.org/10.1515/pac-2014-1117.
[17] M.C. Kreider, M. Sefa, J.A. Fedchak, J. Scherschligt, M. Bible, B. Natarajan, N.N. Klimov, A.E. Miller, Z. Ahmed, M.R. Hartings, Toward 3D printed hydrogen storage materials made with ABS-MOF composites, Polym. Adv. Technol. 29 (2018) 867–873. https://doi.org/10.1002/pat.4197.

Graphical abstract