Monolithic MOFs for Carbon Capture

CCUS Innovation 2.0

Key Knowledge Deliverable 1.1, 1.2 & 3.

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1. Material Selection and Optimisation

Flue gas CO_2 capture technologies aim to directly extract carbon dioxide from industrial exhaust gases, which typically contain CO_2 concentrations ranging from a few to several percent. Given the need for rapid and effective separation in high-throughput environments, these systems rely on materials with exceptional CO_2 affinity to enhance capture efficiency. Selecting the right materials can significantly impact the overall performance and energy demands of the capture process, making material choice a critical factor in optimizing these technologies for sustainable, large-scale CO_2 capture.

Metal-organic frameworks (MOFs) are highly promising materials for carbon capture applications due to their exceptional porosity, tuneable structure, and high surface area. These characteristics allow MOFs to selectively adsorb and store significant amounts of CO_2, even at low concentrations, making them ideal for efficiently capturing carbon from industrial emissions.

One bottleneck in the industrialization of MOFs is the challenge of shaping them into a physical form suitable for deployment in industrial processes. MOFs are typically synthesized as powders, which are difficult to handle and integrate directly into carbon capture systems. To address this, MOFs need to be formed into stable structures, which is often achieved through pelletization. However, pelletizing significantly reduces the accessible surface area of the MOF, which can cut CO_2 capture capacity by as much as half. This trade-off between structural stability and adsorption efficiency remains a key hurdle, underscoring the need for advanced shaping techniques that preserve MOF performance.

A second major bottleneck in the industrialization of MOFs is the tough synthesis conditions required for these materials. Many MOFs are produced under specific, often challenging conditions involving high pressures and temperatures and toxic solvents. These requirements not only increase production complexity but also increase costs, making large-scale manufacturing difficult.

At Immaterial, we have tackled these key challenges in MOF shaping and scale-up by leveraging our innovative, green sol-gel technology to create densely packed monolithic MOF (m-MOF) particles with maximum capacity. This approach allows us to produce robust, high-performance m-MOF structures that retain the superior CO_2 capture efficiency of powdered MOFs while forming mechanically stable bodies of densely packed MOF nanoparticles. The result is a high volumetric capacity that meets the strict demands of industrial applications, providing both efficiency and structural integrity. Densely packed m-MOF beds will make a difference due to their high volumetric adsorption with the potential for a higher density of active material in the bed compared to other alternatives. Increased density allows for a greater amount of MOF material to be packed in a given volume leading to improved adsorption intensity, smaller equipment and footprint, and lower capital cost.

In this project, we have chosen three monolithic metal-organic frameworks (m-MOFs), namely IMM-16, IMM-16h (variants of generation 1 material), and IMM-28 (generation

2 material). The Gen 1 materials feature tetranuclear metal citrate clusters in an octahedral geometry, while the Gen 2 material includes five-coordinated metal centres with a distorted trigonal bipyramidal geometry. (Figure 1). Each of these unique structures includes channels that selectively capture CO_2 over N_2, making it an outstanding candidate for efficient CO_2 capture from flue gases. Additionally, the materials' robust nature addresses stability issues commonly encountered by such materials in humid conditions, further enhancing their suitability for flue gas CO_2 capture.

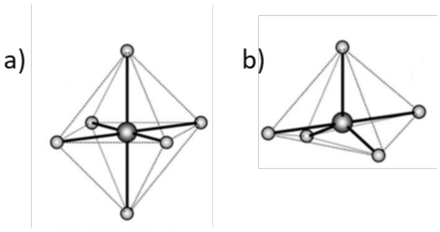


Figure 1: Schematic representation depicting the cluster geometry employed in the formation of generation 1 materials octahedral (a) and generation 2 materials distorted trigonal bipyramidal (b).

In order to develop a scalable recipe, it is necessary to adjust and optimize the synthesis conditions. The initial recipes outlined in the literature utilized substantial quantities of organic solvents. However, to minimise production costs at scale and to improve the safety and operability of the process with large-scale production, our goal has been to replace these solvents with water.

We have aimed to operate at the lowest practical temperatures (below 100°C) whenever feasible, thereby minimizing energy costs on a larger scale and maximizing the efficiency of the process in terms of space-time yield. As a result, we are currently in the stage of exploring different concentration levels to achieve the desired quality of the material at lower temperatures.

With all these optimisations described above we aim to reach a product that demonstrates the anticipated adsorption performance as well as satisfactory density and mechanical stability. These optimizations are currently being carried out at a synthesis scale of 10 ml, to produce approximately 1 g of material and achieve a bulk density ranging between 0.8 and 1.4 g/cm^3.

1.1. Characterisation Methods

CO_2 adsorption and desorption measurements were performed at room temperature using a Micromeritics 3Flex instrument (see below picture). Prior to analysis, samples were degassed at 150 °C for 6 h under vacuum.

Bulk density was obtained through EinScan-SE 3D Scanner. This technique was used to estimate the particle density of monoliths at atmospheric pressure by determining the volume. Prior to the analysis, all samples were activated overnight at 120 °C (vacuum) before measuring the mass.

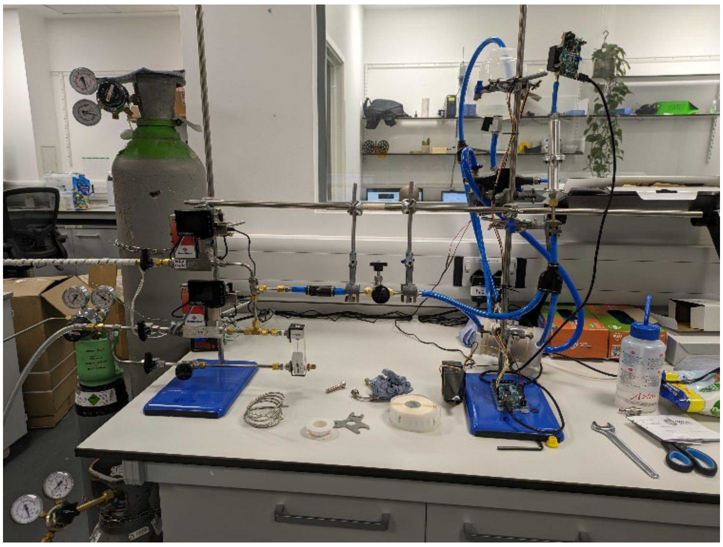
Mecury porosimetry was used also to measure the bulk density. Mercury porosimetry was obtained up to a final pressure of 4,000 bar using a POREMASTER-60 GT instrument from Quantachrome Instruments. Prior to the analysis, all samples were activated overnight at 120 °C (vacuum) before measuring the mass and then degassed in situ thoroughly before the mercury porosimetry.

Vortex shaker was used to test the mechanical robustness of the produced monoliths. Scientific Industries SI™ Vortex-Genie™ 2 was used, with a speed range from 600 to 3200 rpm.

Scanning electron microscopy (SEM) was performed by using a FEI Nova NanoSEM at an acceleration voltage of 3.0 kV. Dried monoliths were prepared for analysis by crushing with a spatula and pressing a copper grid into the resulting powder. Images were processed with Image J software.

Breakthrough analysis has been conducted using an inhouse-built test rig (see below) at 1 bar pressure using CO_2 and N_2 gas mixture at room temperature under dry and wet conditions. The design of a CO_2 capture adsorption system requires an evaluation of the mass transfer kinetics of the adsorption mechanism which can strongly influence the process performance. To quantify the kinetic parameters, a lab-scale breakthrough test rig was constructed from Swagelok components to introduce a controlled gas mixture into a packed bed of MOF (approximately 5 g). On-line monitoring of the inlet flow rates of each component (using Bronkhorst MFCs), and the outlet CO_2 concentration (using an Alphasense NDIR sensor) produces a so-called "breakthrough curve". The shape and gradient of the breakthrough curve are strongly influenced by the mass and heat transfer kinetics of the underlying system and material. Therefore, with appropriate material properties and equilibrium models, the kinetic parameters can be quantified through process simulations.

Monolithic MOFs for Carbon Capture



1.2. Synthesis Optimisation

The synthesis process commenced with a solvent-water mixture as a solvent at a temperature below 100 Celsius. Subsequently, we optimise the solvent quantity and the concentration of the precursors. Through controlled adjustments, we successfully tailored the synthesis of the IMM-16 and IMM-28 crystals. This optimization resulted in the formation of a well-packed monolith with a high yield of up to 85% (Figure 2a), as opposed to the formation of a powdery pellet (Figure 2b).

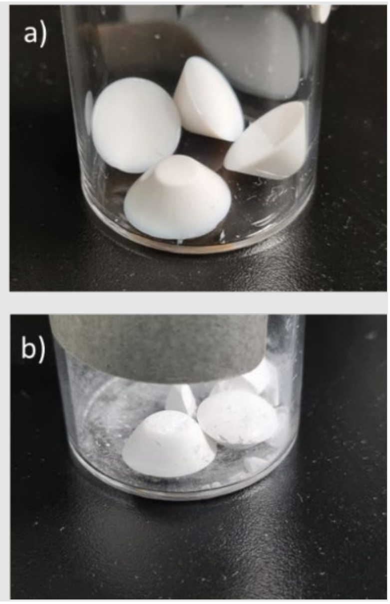


Figure 2: (a) Photo of well particle packed IMM-16 monoliths (b) Photo of powdery IMM-16 pellets.

Then, the efforts focused on understanding the mechanical properties of the IMM-16 monoliths while preserving their adsorption capacity. To do that, a vortex shaker was used to test the mechanical robustness of the produced monoliths. The optimised monoliths were placed in a glass vial and vortexed at 3200 rpm for 10 seconds to test the robustness of the monoliths. We observed the pieces before and after to prove the robustness and measure the weight of the monoliths to quantify the loss of the material due to dusting caused by the vigorous shaking in a glass vial.

The vortex testing showed that we don’t have any disruption on the mechanical stability of IMM-16 after the treatment.

In order to enhance the performance of IMM-16 when exposed to humid streams, we proposed surface functionalization of the monoliths. Thus far, we have successfully observed the hydrophobic behaviour of the IMM-16h by simply adding water on top of the materials. (Figure 4)

Vortex testing of IMM-16h confirmed the mechanical stability of produced monoliths remain as the same after the hydrophobic treatment to create IMM-16h. (Figure 5a)

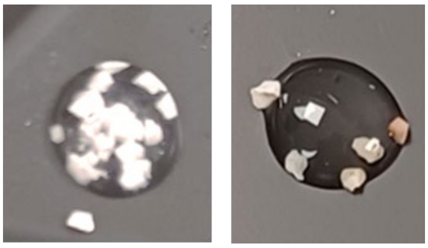


Figure 4: Pictures of IMM-16 (left) and IMM-16h (right) in contact of water. IMM-16h is repelling water when we drop water on the material.

We used a very similar procedure in IMM-28 optimisation to achieve the desired mechanical stability where the produced monoliths had excellent CO_2 adsorption capacity (Figure 5b and 6) as well as measured density of 1.3 g/cm^3 for IMM-16 and IMM-16h, and 1.0 g/cm^3 for IMM-28.

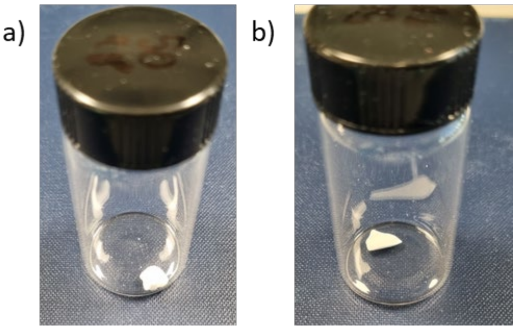


Figure 5: Picture of the vials after the vibration test on a IMM-16h monolith (b) and a IMM-28 monolith (b).

Scanning Electron Microscopy (SEM) images provided valuable insights into the characteristics of the nanoparticle size and the packing density of the particles within the monolithic structures. In our analysis, we focused on the optimized materials, specifically IMM-16 and IMM-28. As illustrated in Figure 6, the particle size for IMM-16 ranged from 500 to 550 nm, while IMM-28 exhibited a larger particle size, measuring between 900 and 950 nm. Additionally, the SEM images revealed the packing arrangement of these nanoparticles within the monoliths.

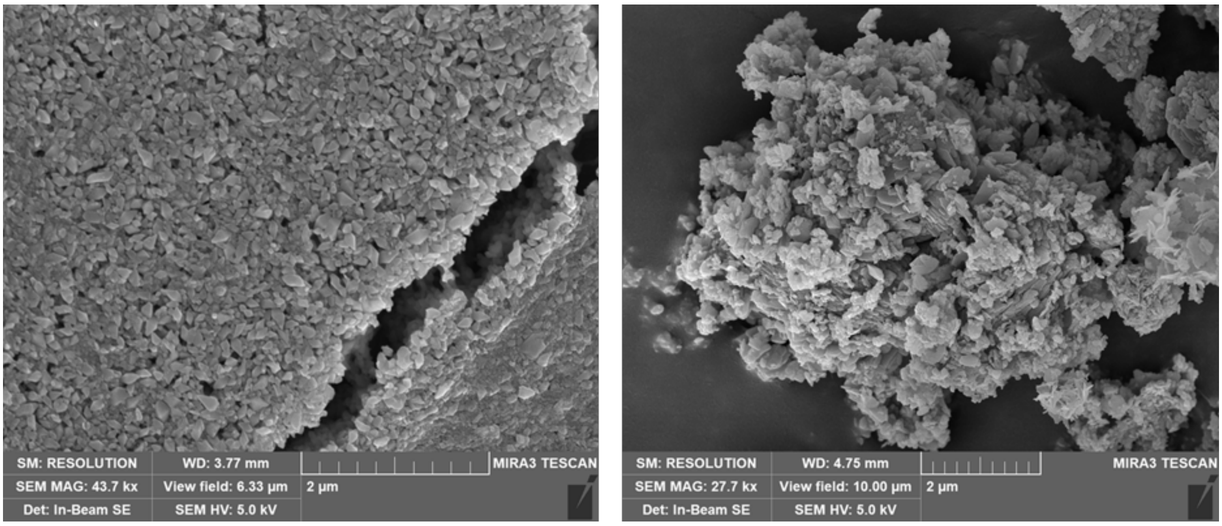


Figure 6: SEM images of monolithic IMM-16 (left) and IMM-28 (right)

As a further characterisation for the particle packing, we measured the bulk density of the materials synthesised. The monoliths have been scanned through a 3-D scanner to determine the bulk volume. Monoliths exhibited a high density varying between 0.8 to 1.3 g cm^{-3}. In the modelling, we used the density values obtained from 3D-scanner as we can do it quickly and accurately at Immaterial facilities. Then, we also measured mercury porosimeter of the optimised samples at University of Alicante in Spain to compare the density calculation we have with another method. (Table 1) Although we have differences of approx. ±0.2 g/cm^3, the trend between materials is the same regardless of different measurement techniques. We don't see any impact of this on the performance modelling compared to the data used obtained by using 3D-scanner.

Table 1. Measured bulk density results were obtained by using a 3D scanner and Hg porosimeter.

	3D-scanner density (g/cm^3)	Hg porosimetry density (g/cm^3)
IMM-16	1.30	1.42
IMM-16h	1.24	1.05
IMM-28	1.0	0.8

Adsorption isotherms are fundamental for characterizing the m-MOF materials, given their microporous nature and significant applications in gas separation. We measured single-component isotherms for both CO_2 and N_2 at various temperatures to evaluate the selectivity of our materials for CO_2 and N_2, as well as to facilitate calculations of the heat of adsorption. The results of these measurements are illustrated in Figure 8, providing critical insights into the performance and efficiency of our m-MOFs in capturing carbon dioxide.

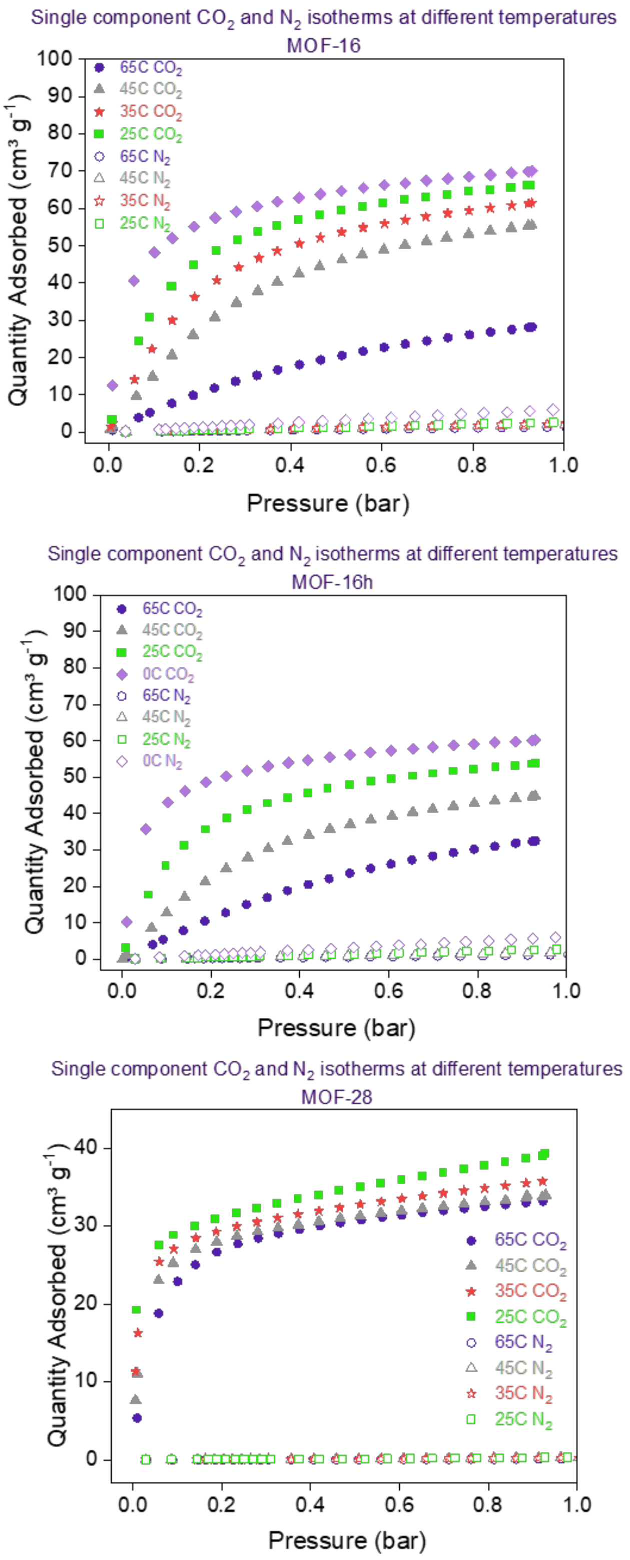


Figure 8: Single component CO2 and N2 isotherms at different temperatures for IMM-16, IMM-16h and IMM-28.

Breakthrough curves provide information about the kinetics of the gas adsorption. The breakthrough time specifically indicates details about convective mass transfer within the bed. The incline of the ascending curve discloses information about intra-particle macropore diffusions, while the region on the left-hand side of the curve typically signifies total gas uptake. In summary, comparing breakthrough curves for various gases yields valuable information regarding the competition among adsorbate molecules within the porous solid.

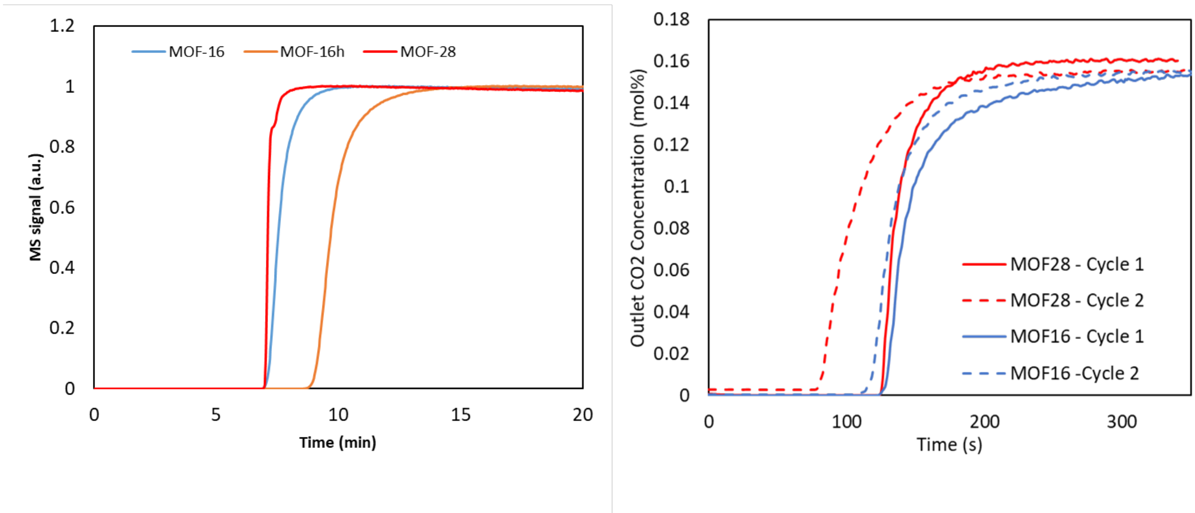


Figure 9. Plots of dry (CO_2 15% and N_2) for IMM-16, IMM-16h and IMM-28 on the left and wet (CO_2 15%, N_2 and 50% RH) breakthrough measurements for IMM-16 and IMM-28 on the right.

Initial analyses of breakthrough measurements for dry (CO_2 15% and N_2) and wet streams (CO_2 15%, N_2 and 50% RH) suggest insignificant mass transfer limitations as illustrated in Figure 4. This behaviour is favourable for the dynamic of a typical VPSA process as it allows the system to achieve faster cycles and higher productivity. (Figure 9)

To check the stability of our materials under moisture, we conducted single component CO_2 isotherm before and after the wet breakthrough testing. We conducted two cycles and performed the CO_2 adsorption analysis for all the samples. As evident from Figure 5, the three selected adsorbents show 5-10 % (IMM-16 and IMM-16h) or no loss (IMM-28) of capacity after being exposed to CO_2 streams with 50% relative humidity.

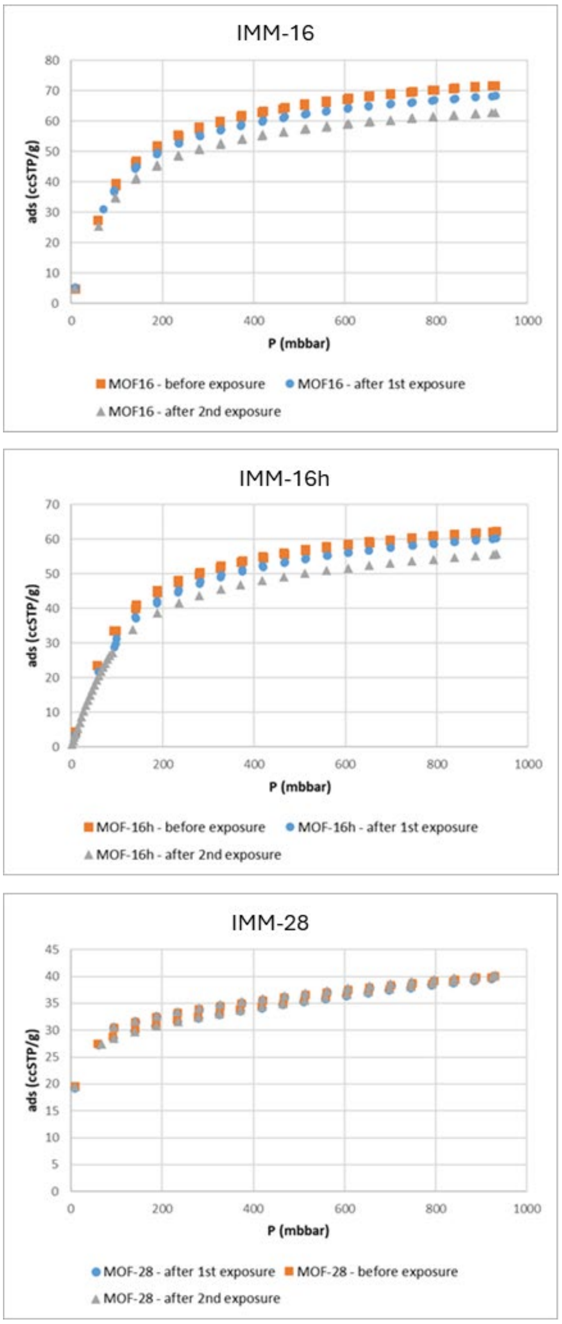


Figure 10. Single component CO_2 isotherms for IMM-16, IMM-16h and IMM-28 before and after exposure to moisture.

2. Generation of Structured Adsorbents

As a further improvement, our second objective in this project is to utilize our m-MOF as shaped adsorbents, capitalizing on their enhanced volumetric capacity. This approach allows us to harness the inherent advantages that shaped adsorbents provide, such as reduced cycle times and improved kinetics in adsorption processes. Additionally, these m-MOFs help minimize pressure drops within the system, leading to more efficient operation. By achieving these objectives, we aim to significantly enhance the efficiency and effectiveness of adsorption systems, making them more viable for large-scale industrial applications and ultimately contributing to more sustainable carbon capture solutions.

We initially used the same formulations that had been developed for monolith production as a starting point in the expectation that they would need to be changed for a new application. The initial trials demonstrated this to be correct, and formulations need to be optimised for the particular shape. A notable challenge arose from their poor mechanical stability, leading to issues like cracking. Through iterative experimentation and refinement, we successfully developed shaped bodies that showed improved mechanical stability.

We conducted multiple screenings, experimenting with the formulation of the sol-gel process. Among these trials, two different exemplar compositions represented by data points 97I and 97J in the plot in Figure 11 emerged as the optimal choice, offering superior mechanical stability while preserving the adsorption capabilities of the shaped IMM-16.

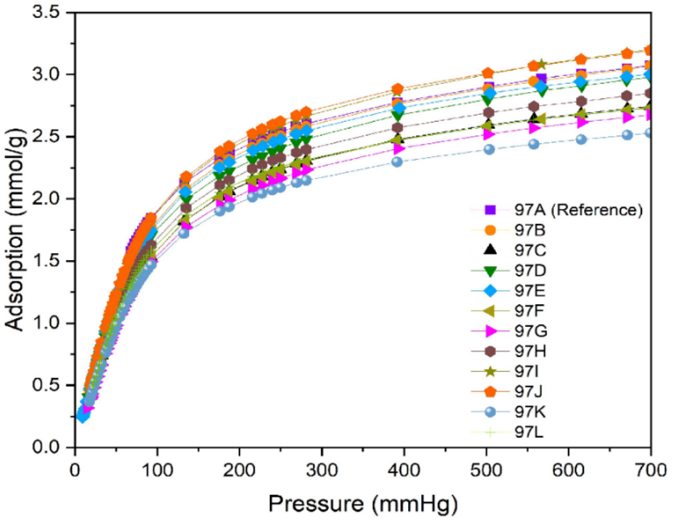


Figure 11: CO_2 adsorption isotherms at 21 °C of IMM-16 shaped adsorbents.

3. Scale-Up of the Optimised Procedures

After the successful small-scale optimisations of IMM-16 and IMM-28, we gradually started the scale-up production from 10 mL up to 30 L in 5 steps (50 mL, 200 mL, 1L, 5L and 30 L) to ensure the material maintains the same properties in each scale-up stage. The production process consists of four different steps: i) batch synthesis, ii) centrifuge washing, iii) drying, and iv) activation at 120 °C under vacuum. For 30 L batch reactions, we have used a large 30 L jacketed reactor with an overhead stirrer (Figure 12a). Heating is done by the oil circulating in the jacket around the reactor at a constant temperature. After the reaction, washing was done using a 750 mL centrifuge, and the materials were dried in the centrifuge buckets. (Figure 12b) After drying the washed MOFs in the buckets, we end up with multi-centimeter size monolith bodies, which we carefully mill to the required particle size. 1.6 to 2 kg of the material can be achieved from a 30 L batch for both materials. Room temperature CO_2

adsorption isotherm of the two samples synthesised in 30 L batch size exhibited a similar CO_2 uptake with compared to small batches. (Figure 13).

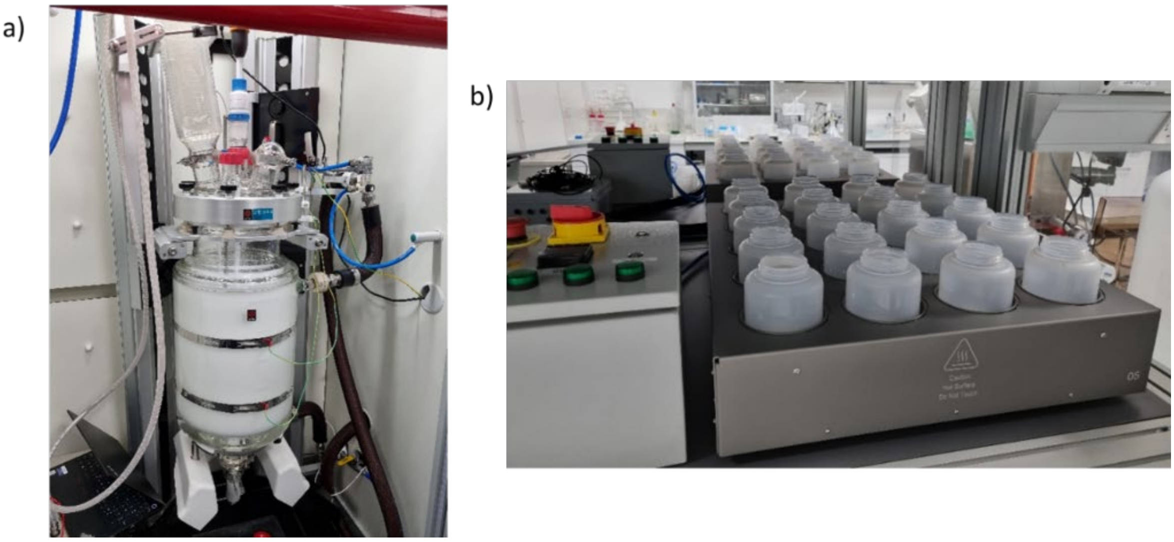


Figure 12: Photos of a large-scale (30 L) reaction (a). MOFs drying in the buckets to produce monoliths. (b)

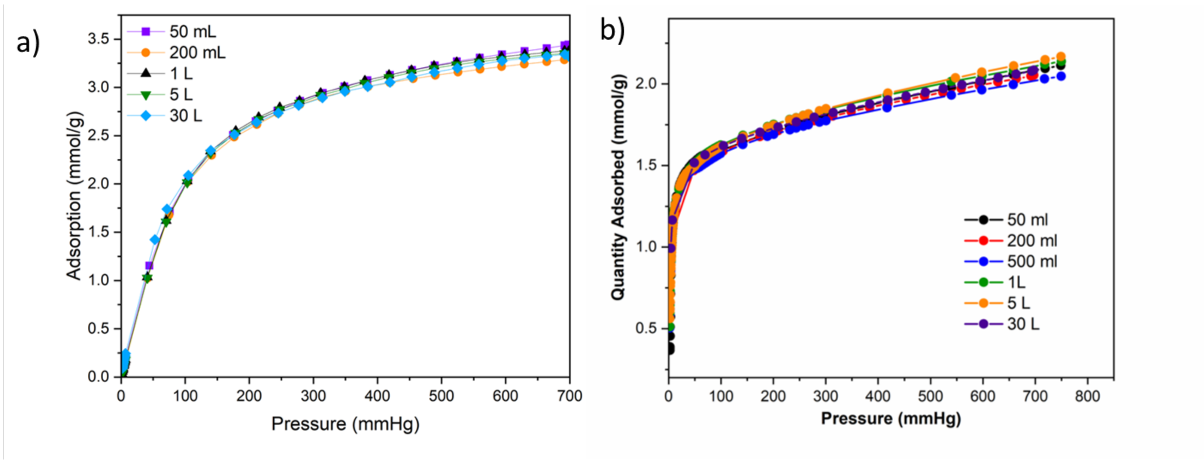


Figure 13: CO_2 isotherms at room temperature for the products produced by different batch size. IMM-16 (a) and IMM-28 (b)

After drying the washed MOFs in the buckets, we end up with multi centimetre size monolithic cakes (Figure 14a). These cakes are highly dense and porous materials ready to be chopped down to any particle size needed by the application. The density measured through the 3D scanner produced by 30 L batch reactor were measured as 1.24 g/cm^3 for IMM-16 and IMM-16h, and 1.06 g/cm^3 IMM-28 are in agreement with the small scale.

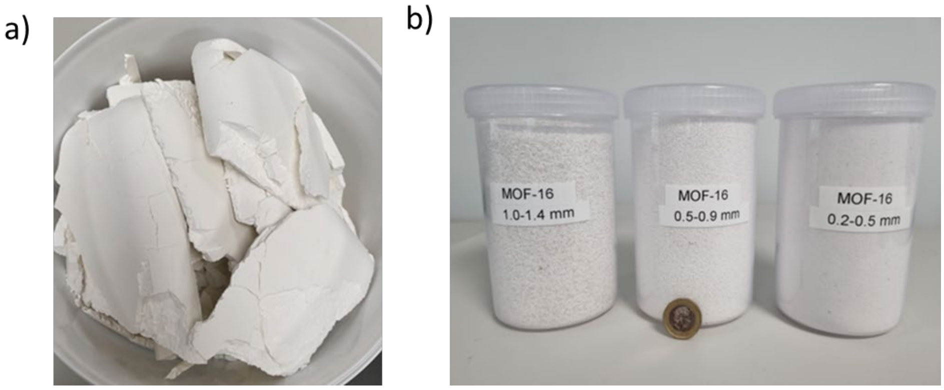


Figure 14: Multi-centimeter sized monolithic IMM-28 cakes (a) and chopped IMM-16 samples to a specific particle sizes (b).

Optimizing particle size in adsorption systems will critically affect balancing the trade-offs between adsorption kinetics and pressure drop. Smaller particles typically offer faster adsorption kinetics due to their larger surface area-to-volume ratio, but they also result in higher pressure drop due to increased resistance to flow. Conversely, larger particles reduce pressure drop but may exhibit slower adsorption kinetics. By systematically investigating the relationship between particle size, adsorption kinetics, and pressure drop, we aim to identify the optimal particle size range that maximizes adsorption efficiency while minimizing energy penalties in our adsorption system.