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Magnetic Framework Composites for CO₂ Capture

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degree of Doctor of Philosophy

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*The Lord is my shepherd, I lack nothing.
He makes me lie down in green pastures,
he leads me beside quiet waters,
he refreshes my soul.
He guides me along the right paths
for his name's sake.
Even though I walk
through the darkest valley,
I will fear no evil,
for you are with me;
your rod and your staff,
they comfort me.*

*You prepare a table before me
in the presence of my enemies.
You anoint my head with oil;
my cup overflows.
Surely your goodness and love will follow me
all the days of my life,
and I will dwell in the house of the Lord
forever.*

This thesis is dedicated first to God, then to my wife and family.

*Great are the works of the Lord;
they are pondered by all who delight in them.*

Psalm 111:2

*For God so loved the world that he gave his one and only Son, that
whoever believes in him shall not perish but have eternal life.*

John 3:16

Abstract

Climate change is possibly the greatest challenge currently facing mankind. Immediate action is required to prevent the most devastating effects, particularly on developing nations. This change is being driven by record levels of atmospheric CO₂, largely emitted during electricity and heat production. A promising solution is post-combustion carbon capture, which can be retrofitted into existing power stations and allows for the capturing of CO₂ at source, removing it from flue gas mixtures. Metal-organic frameworks (MOFs) are highly porous materials consisting of metal ions or clusters linked by organic molecules. MOFs have demonstrated excellent potential for CO₂ capture applications due to their high sorption capacities and selectivities for CO₂ over other gases. However, MOFs are naturally thermal insulators, making thermal regeneration (emptying the MOF after each adsorption cycle for reuse) challenging, especially on the larger scales required in industrial settings. This limitation can be overcome by forming composites of magnetic materials with the MOFs (magnetic framework composites, MFCs) enabling rapid and energy efficient thermal regeneration by magnetic induction heating.

This thesis describes an investigation into the synthesis of a variety of MFCs (with microsphere and nanoparticle magnetic components, and MOFs HKUST-1, SIFSIX-3-Cu and UTSA-16(Zn)) for CO₂ capture by different methods, presented *via* a collection of manuscripts and associated commentaries. Comprehensive characterisation of materials produced (elucidating structure-property relationships) and analysis for CO₂ capture and release performance are contained within the manuscripts.

Chapter 1 (page: 1) first introduces the research area, covering MOFs, MFCs and carbon capture. The associated paper in Appendix 1 (page: 60) reviews the activation and regeneration of MOFs, enabling their high porosities and surface areas to be exploited for sorption applications. Principles of the circular economy and sustainability are considered regarding this process (such as resource and energy efficiency), with a discussion on how these perspectives can inform future developments for MOFs.

Chapter 2 (page: 14) and Appendix 2 (page: 109) describe the production of hierarchically porous MFCs through the layer-by-layer growth of MOFs, specifically HKUST-1 and SIFSIX-3-Cu, on the surface of porous magnetic microspheres (PMMs). A novel flame-spheroidisation route was developed to produce the highly macro-porous PMMs (intraparticle porosity: 95%), which were surface functionalised with molecular and polymeric coatings to facilitate composite formation. Macro-micro hierarchically porous MFCs were then synthesised through a controlled layer-by-layer heterogenous MOF growth strategy (10-11 wt.% MOF loading). This resulted in the first examples of a new material class of MFCs, which contain single-material porous magnetic scaffolds.

Chapter 3 (page: 23) and Appendix 3 (page: 170) explore a microwave-assisted direct growth method for producing MFCs containing citrate-coated Fe_3O_4 nanoparticles embedded in MOF UTSA-16(Zn). A continuous flow hydrothermal synthesis was first developed to produce magnetic nanoparticles in a single-step, with a comparably very high saturation magnetisation of 78 emu/g due to high purity and crystallinity. These nanoparticles were then incorporated into the MOF *via* a rapid microwave-assisted direct growth strategy (optimised for the pristine MOF), forming MFCs (3-19 wt.% Fe_3O_4 in UTSA-16(Zn)) with both high CO_2 adsorption capacities (2.8-3.3 mmol/g) and rapid heating ability in an applied magnetic field (reaching 60 °C in 8 seconds), facilitating energy-efficient CO_2 release.

Work in Chapter 4 (page: 30) and Appendix 4 (page: 209) builds on the MFCs from the previous chapter (Fe_3O_4 with UTSA-16(Zn)), developing a solvothermal continuous flow synthesis to produce the MFCs in a sustainable and scalable manner. The reaction is first optimised for the pristine MOF UTSA-16(Zn), resulting in the first reported continuous flow synthesis for the MOF with a 77-fold increase to the production rate (173 g/h) compared to batch methods. The magnetic nanoparticles were then incorporated into the flow synthesis, producing MFCs with high CO_2 adsorption capacities (3.1-3.5 mmol/g) in flow (3-11 wt.% Fe_3O_4 in UTSA-16(Zn)). We report here the highest production rate reported of any MFC to date (152 g/h), a 12-fold increase on the previous record.

Appendix 5 (page: 258) briefly describes alternative applications of the induction heating analysis methods developed for the MFCs, which resulted in two second-author papers. Experiments conducted herein demonstrated the suitability of different magnetic particles for magnetic hyperthermia treatment, targeting a controlled temperature ramp and isothermal hold at 40-45 °C.

Finally, Chapter 5 (page: 39) summarises the overall conclusions of the thesis and recommends directions for future work such as scale-up, pelletisation and magnetic-induction rig testing.

Declaration

I declare that the work and papers attributed to the author and presented in this thesis were generated from the work done by the author (John Luke Woodliffe), and that this thesis is not submitted in support of an application for any other qualification or degree in this or any other institution.

Signed: 

John Luke Woodliffe

The published manuscripts in Appendix 1 (page: 60) and Appendices 2 and 3 (pages: 109, 170) were published by Elsevier and the Royal Society of Chemistry, respectively. Both allow the reuse of entire published material in a PhD thesis.

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List of publications/presentations

Publications

- **Woodliffe J. L.**, Ferrari B., Ahmed I., Laybourn A.; *Evaluating the purification and activation of metal-organic frameworks from a technical and circular economy perspective*; Coordination Chemistry Reviews, Volume 428, 2021, 213578, <https://doi.org/10.1016/j.ccr.2020.213578>
- **Woodliffe J. L.**, Molinar-Díaz J., Islam M. T., Stevens L. A., Wadge M. D., Rance G. A., Ferrari B., Ahmed I., Laybourn A.; *Rapid synthesis of magnetic microspheres and the development of new macro-micro hierarchically porous magnetic framework composites*; Journal of Materials Chemistry A, 2023, 11 (27), 14705–14719, <https://doi.org/10.1039/D3TA01927F>
- **Woodliffe J. L.**, Johnston A., Fay M., Ferrari B., Gomes R. L., Lester E., Ahmed I., Laybourn A.; *Rapid microwave synthesis of sustainable magnetic framework composites of UTSA-16(Zn) with Fe₃O₄ nanoparticles for efficient CO₂ capture*; Materials Advances, 2023, 4, 5838-5849, <https://doi.org/10.1039/D3MA00351E>
- **Woodliffe J. L.**, Hussein O., Lester E., Ferrari B., Ahmed I., Laybourn A.; *Continuous flow synthesis of MOF UTSA-16(Zn), mixed-metal and magnetic composites for CO₂ capture – toward sustainable and scalable manufacture*; target journal: ACS Sustainable Chemistry & Engineering

2nd author publications

Key contributions, context and paper summaries can be found in Appendix 5 (page:258).

- Molinar-Díaz J., **Woodliffe J. L.**, Milborne B., Murrell L., Islam M. T., Steer E., Weston N., Morley N. A., Brown P. D., Ahmed I.; *Ferromagnetic Cytocompatible Glass-Ceramic Porous Microspheres for Magnetic Hyperthermia Applications*; Advanced Materials Interfaces, 2023, 2202089, <https://doi.org/10.1002/admi.202202089>
- Molinar-Díaz J., **Woodliffe J. L.**, Steer E., Morley N. A., Brown P. D., Ahmed I.; *Optimisation of the Flame Spheroidisation Process for the Rapid Manufacture of Fe₃O₄-Based Porous and Dense Microspheres*; Molecules, 2023, 28(6), 2523, <https://doi.org/10.3390/molecules28062523>

Presentations

- Oral presentation at International Solvothermal and Hydrothermal conference. **Woodliffe J. L.**, Johnston A., Fay M., Ferrari B., Gomes R. L., Lester E., Ahmed I., Laybourn A. *“Sustainable Magnetic Framework Composites for Efficient CO₂ Capture”* (8th International Solvothermal and Hydrothermal Association Conference, ISHA 2023)
- Oral presentation at RSC’s flagship international materials conference. **Woodliffe J. L.**, Johnston A., Lester E., Ferrari B., Ahmed I., Laybourn A. *“Magnetised MOFs – an Attractive Solution to Carbon Capture”* (16th International Conference on Materials Chemistry, MC16 2023)
- Oral presentation at Midlands Materials Chemistry meeting. **Woodliffe J. L.**, Johnston A., Fay M., Ferrari B., Lester E., Ahmed I., Laybourn A. *“Magnetic Nanoparticles in Metal-Organic Frameworks – an Attractive CO₂ Capture Solution”* (Midlands Materials Chemistry 2023)
- Oral presentation at global UK-China conference. **Woodliffe J. L.**, Ferrari B., Ahmed I., Laybourn A. *“Magnetic Framework Composites for efficient CO₂ capture and release* (UK-China UCEER 2022 Engineering for Carbon Zero global PhD conference)
- Poster presentation at European metal-organic frameworks conference. **Woodliffe J. L.**, Johnston A., Fay M., Ferrari B., Gomes R. L., Lester E., Ahmed I., Laybourn A. *“An Attractive Approach to Capturing CO₂ – Magnetised MOFs”* (5th European Conference on Metal Organic Frameworks and Porous Polymers, EuroMOF2023)
- Poster presentation as a finalist at STEM for BRITAIN, a major scientific poster competition held at the House of Commons with Members of Parliament, academics and industry representatives. **Woodliffe J. L.**, Johnston A., Ferrari B., Ahmed I., Laybourn A. *“Magnetic Framework Composites for efficient CO₂ capture and release”* (STEM for BRITAIN 2023, 1st place, Dyson Sustainability Awards)
- Creative display presentation at UK environmental chemistry conference. **Woodliffe J. L.**, Ferrari B., Ahmed I., Laybourn A. *“Designing Magnetic Framework Composites for Carbon Capture”* (EnvChem2021: Chemistry of the Whole Environment Research)
- Poster presentation at international Commonwealth Chemistry conference. **Woodliffe J. L.**, Ferrari B., Ahmed I., Laybourn A.; *“Magnetic Framework Composites for efficient CO₂ capture and release”* (3rd Commonwealth Chemistry Posters – Building Networks to Address the Goals)
- Poster presentation at UK porous materials conference. **Woodliffe J. L.**, Molinar-Díaz J., Wadge M. D., Ferrari B., Ahmed I., Laybourn A.; *“Novel*

macro-micro hierarchically porous magnetic framework composites” (5th Annual UK Porous Materials Conference, Glasgow, 2022)

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List of Abbreviations

bdc	1,4-benzenedicarboxylate
BET	Brunauer-Emmett-Teller
bpdc	biphenyl-4,4'-dicarboxylate
btc	1,3,5-benzenetricarboxylate
dot	2,5-dioxidoterephthalate
DUT	Dresden University of Technology
DUT-4	AlOH(ndc)
DUT-5	AlOH(bpdc)
EDS	energy-dispersive X-ray spectroscopy
HKUST	Hong Kong University of Science and Technology
HKUST-1	$\text{Cu}_3(\text{btc})_2$
ICP-OES	Inductively coupled plasma optical emission spectroscopy
MAA	mercaptoacetic acid
MFC	magnetic framework composite
Mg-MOF-74	$\text{Mg}_2(\text{dot})$
MIL	Materials of Institut Lavoisier
MIL-101(Cr)	$\text{Cr}_3\text{OF}(\text{H}_2\text{O})_2(\text{bdc})_3$
MIP	Mercury intrusion porosimetry
MISA	Magnetic induction swing adsorption
MNP	Magnetic nanoparticle
MNP-CA	Citrate-coated magnetic nanoparticle

MOF	metal-organic framework
MOF-5	$\text{Zn}_4\text{O}(\text{bdc})_3$
MPYR	4-mercaptopyridine
ndc	2,6-naphthalenedicarboxylate
PAA	poly(acrylic acid)
PAM	polyacrylamide
PDA	polydopamine
PFA	Perfluoroalkoxy
PMM	porous magnetic microsphere
PSS	polystyrenesulfonate
PVA	polyvinyl alcohol
PVP	polyvinylpyrrolidone
PXRD	powder X-ray diffraction
SAM	self-assembled monolayer
STY	space-time yield
TEOS	tetraethyl orthosilicate
TGA	thermogravimetric analysis
TSA	temperature swing adsorption
TVSA	temperature vacuum swing adsorption
UiO	Universitetet i Oslo
UiO-66	$\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_6$
UTSA	University of Texas at San Antonio

UTSA-16(Zn)	$\text{C}_{12}\text{H}_8\text{KO}_{14}\text{Zn}_3$
VSA	vacuum swing adsorption
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZIF	Zeolitic imidazolate framework
ZIF-8	$\text{Zn}(\text{C}_4\text{H}_5\text{N}_2)_2$

Chapter 1

Appendix 1 (page: 60): review paper “Evaluating the purification and activation of metal-organic frameworks from a technical and circular economy perspective” (*Coordination Chemistry Reviews*, Volume 428, 2021, 213578)

Paper highlights:

- *MOFs require activating prior to use and regeneration throughout use.*
- *MOF activation/regeneration methods evaluated against circular economy principles such as scalability, waste reduction, material reuse, energy efficiency and environmental impact.*
- *Calcination and solvent exchange are demanding from chemical use, time, and energy perspectives, and harsh conditions can lead to framework collapse.*
- *Framework collapse can be avoided through the use of ultra-low surface tension solvents, supercritical CO₂ or freeze-drying.*
- *Time and energy efficiency improved through ultrasound or targeted heating methods such as microwave, UV–Vis or induction heating.*
- *Future MOF research from laboratory to industrial scale would benefit from recovery and reuse of activation solvents and the use of life-cycle assessments.*

1 Introduction

1.1 CO₂ capture

1.1.1 Drivers

Since the industrial revolution, a sharp increase in atmospheric concentrations of the greenhouse gas carbon dioxide (CO₂) has been observed from 180–280 ppm to over 420 ppm (July 2023)^{1–3}. This increase has significant negative implications for the environment and society⁴, and is predicted by the World Health Organisation to result in 250,000 additional deaths worldwide annually between 2030 and 2050⁵. The Intergovernmental Panel on Climate Change (IPCC) report that, in order to avoid the

worst effects of climate change, the temperature rise must be kept below 2 °C relative to preindustrial levels⁶. This requires greenhouse gas emissions reduced globally by 41-72% by 2050 compared to 2010 (49 GtCO₂eq/yr in 2010)⁶. According to the Global Carbon Capture and Sequestration (CCS) Institute, this would require the number of industrial scale CCS facilities in operation to increase from the current 19 to over 2000 by 2040⁷. Governments around the world are setting net zero CO₂ emissions targets by 2050-2070 in line with the recent report from the IPCC⁸, and have affirmed their commitments in Glasgow 2021 at COP26⁹. Addressing these IPCC targets requires immediate action, preventing CO₂ from entering the atmosphere.

1.1.2 CO₂ capture approaches

The largest contributor to global anthropogenic CO₂ emissions are coal-fired power plants (10.1 Gt in 2018, 30% of total CO₂ emissions)^{10,11}. Currently there are three main approaches for CO₂ capture from power plants, namely post-combustion, pre-combustion and oxy-fuel combustion. Direct air capture is another approach which has been gaining traction more recently.

Post-combustion CO₂ capture

Post-combustion capture separates the CO₂ from the flue gas after fuel combustion. The major advantage of this approach over the others is that post-combustion capture facilities can be retrofitted into existing power stations¹². The CO₂ concentration in the flue gas stream is typically around 15%, with the majority gas being N₂, also containing some H₂O, O₂, CO, NO_x and SO_x¹³. Unfortunately, the current aqueous amine absorption technologies for this process have high energy requirements for separation and purification, increasing a power plant's energy demand by 25-40%¹⁴. These technologies also suffer from amine degradation and equipment corrosion over time¹⁵. Ideal adsorbents require a sustainable and scalable synthesis route, high selectivity for CO₂ over N₂ and other flue gas components, have a high CO₂ capacity, a low energy for separating the CO₂ and regenerating the adsorbent and a high long-term stability¹³. Alternatives to the aqueous amines have been investigated, such as physical sorbents, membranes, chemical looping and solid sorbents (e.g. porous carbons, zeolites, alumina and metal-organic frameworks

(MOFs¹⁴). Of these alternatives, MOFs possess many advantages for industrial-scale carbon capture. One major advantage is a reduced energy for CO₂ regeneration, as the CO₂ is physically adsorbed to the material surface, rather than bound by chemical bonds which would need to be broken to release the CO₂¹⁶ (e.g regeneration energy 1-2.5 MJ/kgCO₂ for a MOF adsorbents¹⁷ and 3-4 MJ/kgCO₂ for amine solvents)¹⁸. Advantages of MOFs over other solid adsorbents include a greater uptake capacity and selectivity for CO₂¹⁶, very high internal porosities and surface areas, adjustable pore sizes and geometries which can tailor selective CO₂ capture for specific atmospheres¹⁹, and versatile modifications to enhance CO₂ capture performance¹⁵.

Pre-combustion CO₂ capture

Pre-combustion capture involves first converting fossil fuels such as coal to a gaseous mixture at high temperature and pressure (mostly H₂ and CO), then the water-gas shift reaction which converts the mixture to H₂ and CO₂. The CO₂ is then separated, before the H₂ undergoes combustion to generate electricity¹³. The higher concentration and pressures of CO₂ in the feed (CO₂ concentration: 15-16% for post-combustion and 25-35% for pre-combustion)¹³, and the greater differences between the polarizability and quadrupole moment of CO₂ and H₂ (pre-combustion) compared to CO₂ and N₂ (post-combustion) makes the separation an easier process²⁰. Typically, continuous membrane-based separation processes are preferred for this technology as they are often more efficient at the high pressures and highly concentrated sources²¹.

Oxy-fuel combustion CO₂ capture

Oxy-fuel combustion is a relatively newer process for CO₂ emission mitigation and involves igniting pulverised fuel in an O₂-only environment, producing mainly CO₂ and H₂O. The water vapour can be condensed leaving a CO₂ stream ready for capture. The main challenge and energy penalty for this process is the large-scale separation of air to generate pure O₂²².

Direct air capture

Direct air capture is a negative carbon technology which captures CO₂ from the approximately 400 ppm concentration present in the air. The major advantage of this

process is the ability to capture CO₂ emitted from distributed sources (not just point sources), which make up around half of total CO₂ emissions²³. Challenges remain around finding adsorbents which can effectively capture CO₂ at such low concentrations and at variable humidity (0-100%), and developing highly efficient gas/sorbent contacting strategies to make the process economically viable²³.

1.1.3 CO₂ regeneration

In any adsorbent-based CO₂ capture process, after each adsorption cycle the adsorbent must be regenerated to prepare for the next cycle. The recovered CO₂ can then be stored or utilised further, such as through conversion to chemicals or energy products²⁴. Regeneration of solid adsorbents can be grouped into three main alternative or overlapping processes: temperature swing adsorption (TSA), pressure swing adsorption (PSA) and vacuum swing adsorption (VSA). The adsorbent will typically be packed in a column/bed, with the temperature and pressure of the bed being adjusted each cycle¹³. An ideal regeneration process will involve minimum energy input to remove the CO₂ without causing degradation or impacting the adsorption performance of the next cycle. TSA processes involve heating the adsorbent to drive off CO₂, adjusting the sorption equilibrium. PSA and VSA regeneration processes release CO₂ by dropping the pressure relative to adsorption. For PSA, adsorption happens at an elevated pressure, while for VSA, adsorption occurs around ambient pressure²⁵. In pre-combustion capture, since the gas stream is already pressurised, PSA is expected to be most appropriate. For post-combustion capture, the energy penalty of compressing the gas or applying a vacuum is quite high, so TSA is likely to be the most viable process. Low-grade heat from the power plant could be used as a source of energy for TSA regeneration, making the TSA process particularly promising²⁶. Energy and time efficient electrified heating processes for TSA, utilising magnetic induction heating, have also been explored for magnetic composite materials such as Zeolite 13X/Fe₃O₄^{27,28} and N-doped porous carbon/Fe₃O₄²⁹, increasing desorption rates by an order of magnitude (103 mg/g min at 171 A)²⁷.

1.2 Metal-organic frameworks (MOFs)

MOFs are a class of porous coordination polymers consisting of metal ions or clusters as nodes and organic molecules as linkers³⁰. As a result of their tuneable natures and high internal surface areas (up to 7800 m²/g)³¹, MOFs have been proposed for wide-ranging applications such as in selective gas adsorption and separation²⁰, hydrogen storage³², fuel cells³³, artificial photosynthesis and solar energy conversion³⁴, as chemical sensors³⁵, catalysis³⁶, drug delivery and biomedicine³⁷, and more³⁸. Some MOFs have now emerged onto the commercial market via, for example, BASF³⁹ and university spin out companies such as Promethean Particles⁴⁰, with products in areas such as toxic gas storage, food preservation, and antimicrobial coatings⁴¹. MOF synthesis techniques have been well reviewed in the literature^{42,43}, with scalability and sustainability assessments also being made^{44,45}.

1.2.1 Activation and regeneration of MOFs

Key to the applications of MOFs (such as gas adsorption/CO₂ capture) is their permanent porosity, as such the final steps in MOF synthesis are purification and activation. During purification and activation the important high surface area is made available by removing pore blocking agents (*e.g.* solvent or other chemicals, such as modulators, used during the synthesis) from the pores of the framework⁴⁶. This has traditionally been challenging, as during activation the structural integrity of the MOF can be compromised and framework collapse can occur, resulting in a loss of porosity and ultimately a drastic reduction in the usefulness of the material⁴⁶. Although significant progress has been made in overcoming pore collapse for established activation procedures such as solvent exchange, supercritical carbon dioxide processing, and freeze drying, exemplified by successful activation of several frameworks^{47–49}; their contribution towards the sustainability and scalability of overall MOF production is largely neglected. These routes typically involve significant energy and solvent consumption. Recently technologies such as microwave heating, UV-Vis irradiation, and ultrasound treatment have been explored for MOF purification and activation^{50–52}. Though these routes offer improved energy efficiency, further optimisation is needed to realise an environmentally and economically sustainable MOF production route required by industry⁵³.

Related to the activation process is the regeneration of MOFs for applications where trapped guest molecules need to be removed so the MOF can be reused; for example in gas separation applications¹⁶ and environmental remediation⁵⁴. Energy efficient heating methods such as magnetic induction heating have been explored for MOF regeneration, whereby an alternating magnetic field was used for controlled desorption, first shown with zeolites, silica, and activated carbon⁵⁵. In a process coined 'Magnetic Induction Swing Adsorption' (MISA), composites of MOFs with ferrimagnetic nanoparticles can be heated for the release of captured carbon dioxide⁵⁶. Potential issues could be slow heat transfer from the nanoparticles to the MOF, then slow transfer through the MOF, or damage caused to the MOF from the heating. However, these have not been observed in practice, with MISA demonstrating very high time and energy efficiency (240 s regeneration at a 42 mT field), promising for industrial scale use^{57,58}. MISA can also be combined with a UV light irradiation method resulting in record levels of 96.8% of adsorbed carbon dioxide being released on demand (MISA alone gave 89.4% release)^{59,60}. The MISA process has also found successful application in methane separation and adsorption from landfill gas⁶¹, and oxygen capture and delivery⁶². From a sustainability perspective this localised heating method is much more time and energy efficient compared to traditional heating alternatives, requiring less energy and operational costs.

The first published paper in this thesis⁶³ (Appendix 1, page: 60) identifies that the activation and regeneration steps are a key part of MOF/MOF-composite applications, including in pollutant gas capture. Despite MOF activation mentions in a few more recent reviews (2017⁶⁴, 2018⁶⁵), the last full review on the topic was 2013⁴⁶. In addition to new technological developments, sustainability and circular economy perspectives particularly had not previously been considered. In the paper in Appendix 1, we critically reviewed the state of the art in MOF purification and activation techniques (including calcination⁶⁶, solvent exchange⁶⁴, supercritical CO₂⁶⁷, freeze-drying⁶⁸, microwave heating⁶⁹, ultrasound⁷⁰, UV-vis⁷¹, induction heating⁵⁶ and acid treatment⁷²) by comparing their technical benefits and challenges against principles from the circular economy model and 'twelve principles of circular

chemistry⁷³. Considerations for scalability, waste reduction, material reuse, and energy efficiency were also evaluated. Calcination and solvent exchange techniques were demanding in terms of chemical use, time, and energy. The harsh conditions required could also lead to structural collapse of the MOF. This collapse could be avoided by solvent exchange with an ultra-low surface tension solvent or supercritical CO₂ prior to activation, or through freeze-drying activation. The use of ultrasound and targeted heating methods such as microwave, UV-Vis or induction heating for activation further improved the time and energy efficiency. We also discussed how a circular economy approach could inform the design and manufacture of future economically and environmentally sustainable MOF purification and activation processes. These processes are key to realising the immense opportunities across a range of applications offered by these materials and their composites. As such, the review served as a guide for progressing the area by identifying future research and development opportunities, such as recovery and reuse of activation solvents and life-cycle assessments.

Since being published in early 2021, the review has received 18 citations (August 2023), particularly from others interested in progressing sustainability considerations around the synthesis and applications of MOFs^{74–78}, including for CO₂ separation and reduction^{79,80}. Some progress has also been made to advance MOF activation and regeneration techniques, in particular Mohamed *et al.* utilised high-throughput computation analysis to better understand and predict structural collapse in copper paddlewheel MOFs⁸¹. Other notable advances since this publication includes a chloride salt treatment for improved activation and recyclability of UiO-66 type MOFs, which increased catalytic activity for oxidative desulfurization processes from 62% to 97% (UiO-66(Zr) after TiCl₄ treatment)⁸². An improved solvent exchange activation process with liquid dimethyl ether was also discovered, which could successfully activate MOFs with coordinatively unsaturated sites and non-coordinatively unsaturated sites, displacing solvent molecules occupying the pores of the MOF as well as those coordinated to metal centres, reducing evacuation temperatures⁸³. Reviews have also been published on specific regeneration strategies for MOFs post acidic-gas capture (temperature and pressure swing,

solvent exchange and UV irradiation)⁸⁴ and on regeneration and lattice reconstruction for MOFs to regain their initial activities⁸⁵. These developments complement and support the work in Appendix 1, developing specific strategies to address activation/regeneration challenges in certain MOFs. However, solvent recovery in activation procedures and more developed life-cycle assessments are yet to be fully explored.

Circular economy

The circular economy is a topical economics model aimed towards sustainable development⁸⁶. It seeks to balance considerations of society, the economy and the environment through principles such as waste prevention and life cycle assessment. Its application to the chemical industry has led to the development of the field of sustainable and circular chemistry and chemical engineering, where resource and energy efficiency are key factors when evaluating research at all levels⁷³. Improving the scalability and sustainability of MOF activation and regeneration techniques by applying principles of the circular economy (such as waste reduction, material reuse and energy efficiency) would significantly contribute towards industrial scale production of MOFs, allowing their property benefits to reach real-world applications. Opportunities for circular processing such as the reuse of chemicals used in the purification, activation and regeneration steps would hugely benefit large-scale production by reducing cost, waste, and environmental impact.

1.3 Magnetic framework composites

Magnetic framework composites (MFCs) are an exciting group of materials comprising both MOFs and room temperature magnetic materials⁸⁷. By combining the unique benefits and applications of MOFs with the advantages of magnetism, the resulting MFCs have become a highly attractive area of research⁸⁸. Some of the advantages of MFCs over pristine MOFs include: energy-efficient localised induction heating for MOF synthesis or regeneration (e.g. heating to 96 °C in 5 min using a 39 mT magnetic field for the synthesis of PCN-250)⁸⁹, enhanced thermal stability, simple magnetic-field induced separation, and magnetic field assisted fluidisation^{87,89–91}. Typical magnetic materials used are nanosized iron-oxides⁸⁷, due to the high

magnetisation (218 emu/g)⁹² and abundance of iron compared to other elements (32.1% of the earth's mass)⁹³. One such example is in the development of materials to capture carbon dioxide from flue gas. Hill *et al.* showed that attaching MOFs, such as Mg-MOF-74 or UiO-66, to magnetic nanoparticles (0-8 wt.% nanoparticles)^{56,58} provides an energy-efficient method to desorb captured CO₂ from within the saturated MOF using rapid, localised magnetic induction heating⁵⁷. These MFCs demonstrated remarkably low carbon capture energy costs, 1.29 MJ/kgCO₂¹⁷ compared to 3-4 MJ/kgCO₂ for amine solvents¹⁸. Crucially, this method also overcame the challenge of the thermally insulating nature of MOFs, which makes standard thermal CO₂ regeneration challenging, especially at scale⁹⁴. Another example is from Yan *et al.* who used MIL-101(Cr) with functionalised magnetic microparticles for the magnetic solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples⁹⁵. Further applications of MFCs in environmental remediation, adsorption, sensing, biomedicine and catalysis, alongside preparation strategies for forming these composites are discussed at length in the literature^{54,87,96,97}.

1.3.1 Magnetism

Magnetic flux density in a material (B) is determined by a combination of any applied magnetic field (H) and the magnetisation (magnetic dipole moment per unit volume) of the material (M). Diamagnetic materials show a weak magnetisation due to paired electrons which will repel an applied field. Paramagnetic materials exhibit stronger magnetisation due to the spins of unpaired electrons, which will align with an applied field. In the absence of an applied field, the spins of paramagnetic materials will be randomly aligned. Below a critical temperature (T_c), spins in magnetic domains may align parallel to each other (ferromagnetic), antiparallel to each other cancelling each other out (antiferromagnetic) or antiparallel to each other without cancelling each other out (ferrimagnetic). Fe₃O₄ is often used in the production of MFCs, and its structure is an inverse-spinel ferrimagnet. When formulated as nanoparticles (3-50 nm), each particle can contain a single magnetic domain. This gives rise to a property known as super-paramagnetism, where magnetic domain spins randomly flip under the influence of temperature, even below T_c, giving the appearance of

paramagnetism whilst maintaining the high magnetisation of a ferrimagnet under an applied field.

Induction heating occurs due to an alternating magnetic field, which can induce eddy currents which flow through the material's resistance to generate heat. In ferro/ferri-magnets, heating also occurs due to magnetic hysteresis losses from domain wall motions. Super-paramagnets have little/no hysteresis, so the predominant heating mechanism for them is Neel relaxation (switching magnetic moment direction)⁹⁸.

1.3.2 Functionalisation procedures

In order to form composites such as MFCs, containing MOFs with magnetic materials, there is often a need to functionalise the surface of the non-MOF component to allow the MOFs to form a strong attachment⁹⁹. Broadly speaking there are four approaches for the non-MOF component: bare (unfunctionalised), built-in functionality (during manufacture), self-assembled monolayer (SAM) formation, and polymer encapsulation. These routes can affix functional groups such as -COOH or -NH₂ to the surface of the non-MOF component, facilitating the formation of strong chemical bonds with MOFs during the formation of composites. Table 1 summarises these techniques, detailing the advantages and challenges for each, alongside appropriate examples from the literature.

Table 1: Comparison of functionalisation techniques for the formation of MFCs

Functionalisation technique	Method for magnetic component	Reported examples	Advantages	Challenges
Bare	No functionalisation	Fe₃O₄ NPs with DUT/HKUST-1 MOFs (COOH linkers interact with Fe₃O₄)¹⁰⁰	No need to functionalise magnetic component	Often weak interactions with MOFs, composite can come apart
Built-in functionality	Functionalised in manufacture by incorporating appropriate reagents	- Fe₃O₄ NPs with Mg-MOF-74. NPs functionalised with COOH groups using trisodium citrate¹⁰¹ - Fe₃O₄ particles with HKUST-1. Functionalised with PAA¹⁰²	No need to treat the magnetic component after manufacture	May not be suitable for some material manufacturing methods
SAM on surface	Manufactured then functionalised by reaction with a SAM	- Fe₃O₄ NPs with MOF-5. NPs functionalised with TEOS then reacted with an amino silane to get amino functionalisation¹⁰³ - Fe₃O₄@SiO₂ microspheres with MIL-101(Cr). Functionalised with TEOS⁹⁵ - Fe₃O₄ NPs with HKUST-1. NPs functionalised with MAA¹⁰³	Can form strong covalent linkages	Forming the SAM on the surface, with strong adsorption of head groups
Polymer encapsulation	Manufactured then functionalised by encapsulation in a polymer	- NPs with ZIF-8. Encapsulated with PVP¹⁰⁴ - Au, Fe₃O₄ and other NPs with ZIF-8, UiO-66, MIL-101(Fe). Coated with PDA^{105,106} - Fe₃O₄ particles with ZIF-8. Coated with PSS¹⁰⁷	Simple coating procedures, wide applicability	Forming a uniform coating around material; Need favourable interactions with the polymer

HKUST-1 = Cu₃(btc)₂, btc = 1,3,5-benzenetricarboxylate; DUT-4 = AlOH(ndc), ndc = 2,6-naphthalenedicarboxylate; DUT-5 = AlOH(bpdc), bpdc = biphenyl-4,4'-dicarboxylate; Mg-MOF-74 = Mg₂(dot), dot = 2,5-dioxidoterephthalate; PAA = poly(acrylic acid); SAM = self-assembled monolayer; MOF-5 = Zn₄O(bdc)₃, bdc = 1,4-benzenedicarboxylate; TEOS = tetraethyl orthosilicate; MIL-101(Cr) = Cr₃OF(H₂O)₂(bdc)₃; MAA = mercaptoacetic acid; ZIF-8 = Zn(C₄H₅N₂)₂; PVP = polyvinylpyrrolidone; PAM = polyacrylamide; UiO-66 = Zr₆O₄(OH)₄ octahedra with bdc linkers; PDA = polydopamine; PSS = polystyrenesulfonate

1.3.3 MFC formation techniques

Numerous techniques for forming MOF composites and hybrids have been identified in the literature, combining the properties of MOFs with a range of other materials

such as metal and metal oxide nanoparticles (NPs), porous carbons, films and membranes, polyoxometalates, enzymes, polymers, oxides and others.^{90,109} Applications and techniques for forming these composites have been discussed at length in the literature^{87,96,97}, and those applicable to MFCs are briefly introduced here. After the functionalisation of the non-MOF magnetic component, there are various methods for growing or attaching the MOF to the material. These include direct growth, secondary growth, layer-by-layer growth and direct mixing. The different growth methods are illustrated by the simple schematic in Figure 1. The most appropriate technique for composite preparation will depend on the properties of the material being joined to the MOF, as well as the chemical properties of the MOF itself. The most applicable of these techniques for MFCs are discussed in Table 2, with explanations of their methods, considerations of advantages and challenges and relevant examples from the literature.

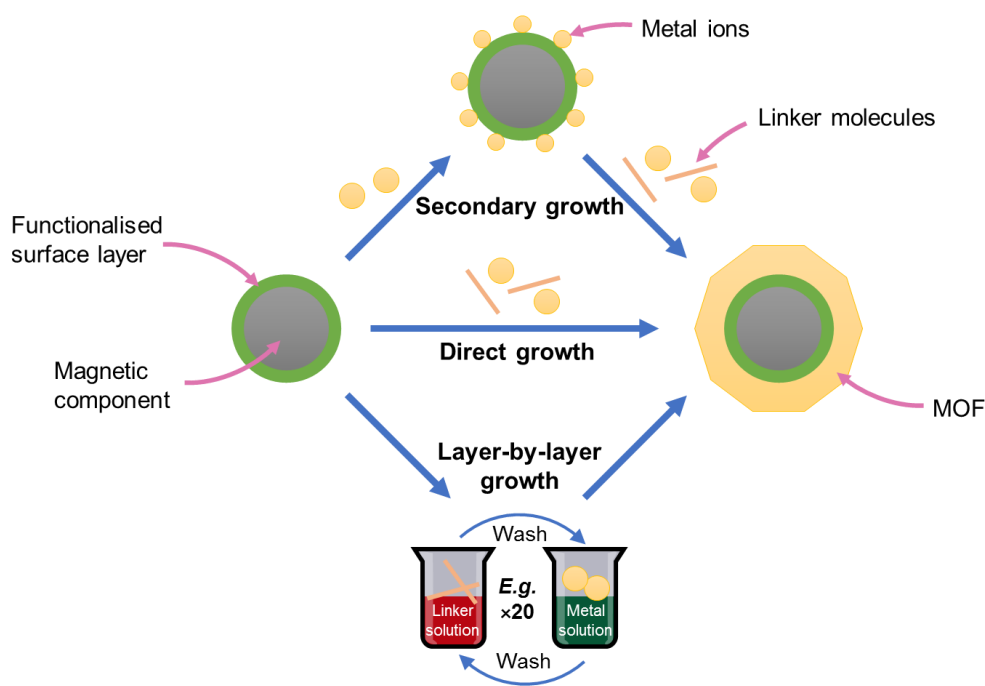


Figure 1: Schematic showing comparison of direct growth, secondary growth and layer-by-layer growth composite formation techniques.

Table 2: A comparison of composite formation techniques for the synthesis MFCs

Composite technique	Method	Literature examples	Advantages	Challenges
Direct growth	Dispersing the magnetic particles in a MOF mother batch solution, allowing the MOF to grow around the magnetic particles	PVP coated Fe₃O₄ NPs in ZIF-8 mother solution¹⁰⁵	Can synthesise MOF with a known method, Low number of synthesis steps	Competing with homogeneous MOF nucleation
Secondary growth	Seeding the surface of the magnetic particles with linker molecules, metal ions or a small volume of MOF crystals, from which the bulk MOF is then grown	Fe₃O₄ mixed with COOH containing linker, then with metal solution for HKUST-1 or DUT MOFs¹⁰⁰	Homogeneous MOF dispersion around magnetic particles	Finding effective seeding conditions prior to bulk MOF growth
Layer by layer growth	Sequentially moving the magnetic particles between solutions of the MOF metal ions and the MOF linker molecules	- HKUST-1 films grown on COOH functionalised magnetic silica NPs (60 cycles)¹¹⁰ - HKUST-1 grown on MAA functionalised Fe₃O₄ NPs (20 cycles)¹⁰⁴	Excellent control of MOF growth	Many synthesis steps, thin MOF coatings
Direct mixing	Pre-synthesised MOFs and magnetic particles are mixed together	TEOS functionalised SiO₂ on Fe₃O₄ microspheres mixed with MIL-101(Cr)⁹⁵	Can synthesise MOF with a known method, Low number of synthesis steps	Forming strong interactions between the MOF and magnetic particle

PVP = polyvinylpyrrolidone; ZIF-8 = Zn(C₄H₅N₂)₂; HKUST-1 = Cu₃(btc)₂, btc = 1,3,5-benzenetricarboxylate; DUT-4 = AlOH(ndc), ndc = 2,6-naphthalenedicarboxylate; DUT-5 = AlOH(bpdc), bpdc = biphenyl-4,4'-dicarboxylate; MAA = mercaptoacetic acid; TEOS = tetraethyl orthosilicate; MIL-101(Cr) = Cr₃O(H₂O)₂(bdc)₃, bdc = 1,4-benzenedicarboxylate

Chapter 2

Appendix 2 (page: 109): paper “Rapid synthesis of magnetic microspheres and the development of new macro-micro hierarchically porous magnetic framework composites” (*Journal of Materials Chemistry A*, 2023, 11 (27), 14705–14719)

Key novelty:

- *Production of highly porous (intraparticle porosity: 95%) magnetic microspheres (diameter: $206 \pm 38 \mu\text{m}$) via a rapid and scalable flame spheroidisation process.*
- *Surface functionalisation of microspheres with molecular and polymeric coatings (0.7-1.2 wt.% loading).*
- *Formation of macro-micro hierarchically porous MFCs through a controlled layer-by-layer heterogenous MOF growth strategy (HKUST-1 and SIFSIX-3-Cu, 10-11 wt.% MOF loading, 36-61% MOF surface coverage on the microspheres).*
- *New material class of MFCs using single-material porous magnetic scaffolds.*

2 Hierarchically porous magnetic framework composites

2.1 Context

In Chapter 1 (page: 1) solid adsorbents such as MOFs were identified as promising materials for post-combustion carbon capture. The challenges and importance of the regeneration step for releasing CO₂ after adsorption so that the MOF can be reused were also discussed. The formation of MFCs was then recognised as a potential solution to the barrier of low thermal conductivities in MOFs, facilitating an energy-efficient heating mechanism (via a magnetic field) for a TSA process (MISA). As discussed in Appendix 2 Introduction (page:112), reported development work with MFCs had almost exclusively involved iron-oxide nanoparticles as the magnetic components⁸⁷. It was therefore decided to explore instead a novel class of MFCs, using single-material porous magnetic scaffolds (porous magnetic microspheres,

PMMs). These microspheres would avoid potential safety concerns over the use of nanoparticles^{111,112}, and offer additional advantages such as: improved flow properties and avoidance of particle agglomeration, beneficial for powder handling and scale-up; more sustainable microsphere synthesis route compared to typical nanoparticle syntheses; potential avoidance of the need for granulation/pelletisation in industrial applications; and hierarchical porosity when combined with other porous materials such as MOFs, demonstrated to benefit many applications such as adsorption, separation and catalysis^{113–115}.

2.2 Summary

The paper in Appendix 2 (page: 109) details an investigation into the synthesis and characterisation of hierarchically porous MFCs (Figure 2). Firstly, a rapid, cost-effective and scalable single-stage flame spheroidisation technique is detailed for the sustainable production of both high porosity (iron/calcium oxides, 95% intraparticle porosity, pore diameter: $12.4 \pm 13.4 \mu\text{m}$) and low porosity (magnetite, 52% intraparticle porosity) magnetic microspheres in the size range of 50 to 300 μm . These are suitable for a wide range of applications, particularly catalysis and environmental remediation, benefiting from ease of detection, efficient separation by magnetic fields, and rapid induction heating capability ($\approx 80^\circ\text{C}$ rise over 30 s at 120 W), with high ambient-temperature magnetisation (M_s : 25-91 emu/g, *cf.* pure magnetite M_s : 94 emu/g). Imparted porosity also offers additional benefits due to the high surface areas and low densities produced, which can enhance applications involving the encapsulation of substances (e.g. pollutants).

Secondly, the creation of innovative MFC materials formed from the PMMs with an archetypal MOF, HKUST-1, and pioneering carbon-capture MOF, SIFSIX-3-Cu, are described. The PMMs were surface-functionalised with polymer and SAM coatings (0.7-1.2 wt.%) prior to MOF growth, and a novel tailored approach of matching the SAM functional group to the MOF linker improved MOF loading for SIFSIX-3-Cu. A controlled layer-by-layer heterogeneous MOF growth strategy was then used on the functionalised PMMs to form MFCs with HKUST-1 (10 wt.% loading, 36 % surface

coverage) and SIFSIX-3-Cu (11 wt.% loading, 61 % surface coverage). These are the first examples of MFCs using a single-material porous magnetic scaffold.

A range of advanced and complementary techniques were used to characterise and evaluate the properties of the MFCs, including Kr sorption and mercury intrusion porosimetry to evaluate hierarchical porosity, confocal Raman microscopy and EDS analysis to map out coverage of the porous scaffolds with the MOF, and vibrating sample magnetometry and heating under induction to evaluate magnetic properties.

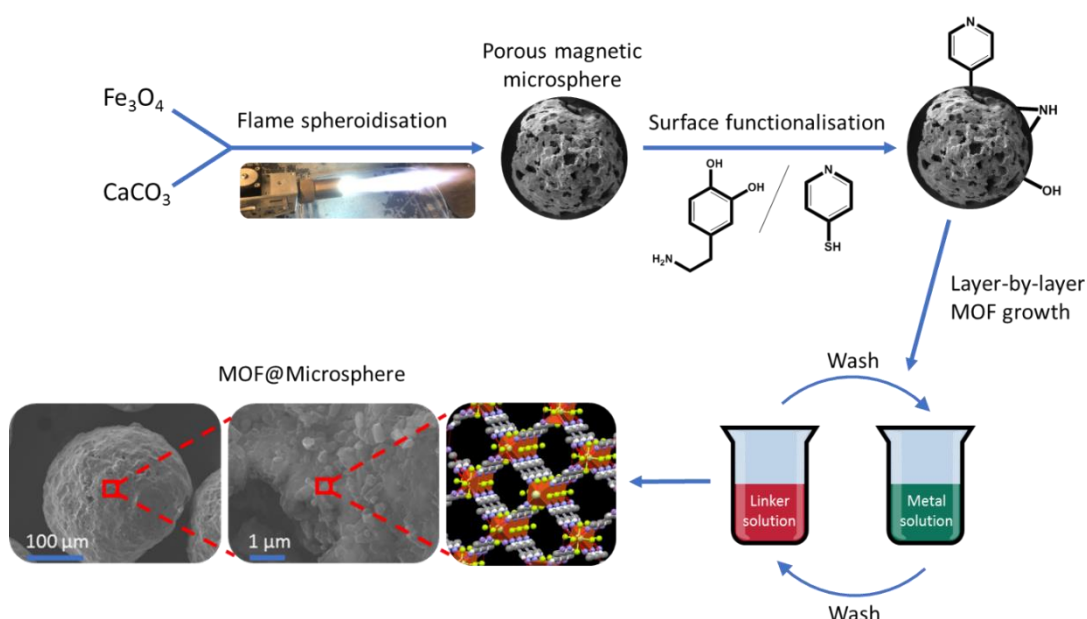


Figure 2: Schematic showing formation of magnetic framework composites from porous magnetic microspheres and metal-organic frameworks via a layer-by-layer method.

2.3 Commentary and critical analysis

2.3.1 Magnetic microspheres

The study begins with a focus on the magnetic component of the final MFCs. The initial aim was to develop and optimise a method for separately producing both high porosity (95%) and low porosity (52%) magnetic microspheres using a rapid and scalable flame spheroidisation process (Figure 3). High porosity microspheres were developed through the inclusion of a porogen (CaCO_3) alongside the Fe_3O_4 in the granulation process, which wasn't present in the synthesis of low porosity microspheres. The granulation process occurs prior to flame spheroidisation, preparing the powders for processing. Production of the low porosity microspheres

required little optimisation, so efforts focused on introducing porosity, beneficial due to high surface areas, low densities and encapsulation capabilities. During porosity development, parameters such as flame collection distance, ratios of starting materials, particle sizes, and grinding durations and methods were investigated. In addition to increasing porosity, a further aim was to minimise the amount of non-magnetic calcite or calcium oxide formed, which would increase mass without contributing to the magnetic properties. As discussed in Appendix 2 section 3.1 (page: 120), the largest effect on porosity resulted from the grinding method and grinding duration of Fe_3O_4 with CaCO_3 prior to granulation and flame processing. The optimum grinding conditions to maximise microsphere porosity (a high number of surface pores in addition to internal pores) was 5 min in a ball mill (500 RPM), possibly due to optimal CaCO_3 mixing and distribution within the Fe_3O_4 granules. During the Fe_3O_4 melting and CaCO_3 decomposition steps of flame processing, CO_2 escapes forming pores while the microspheres cool and solidify.

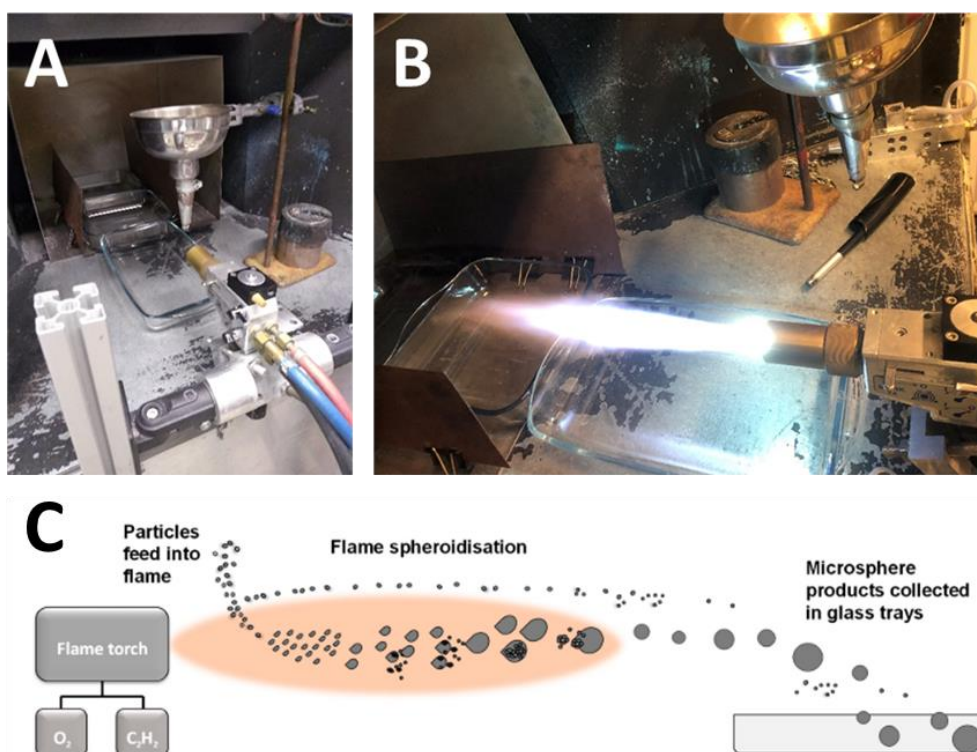


Figure 3: A: Photo of the flame spheroidisation equipment set-up, including the collection trays, flame gun and powder feeder. B: Photo of the flame gun in operation. C: Schematic of the flame spheroidisation process, taken from reference¹¹⁶.

Although the flame spheroidisation process is indeed rapid, a limitation of this method is the extra powder processing steps required prior to flame spheroidisation (grinding and granulation). The scalability and sustainability of these additional steps must be considered when comparing the flame spheroidisation to alternative processes of producing microspheres. Indeed, powder grinding and wet granulation methods are ubiquitous in industry^{117,118}, so these steps may not hinder the scalability of the whole process, however they are energy-intensive. The yield of spheroidisation (76-84%) can also be improved by optimising how granules are injected into the flame, and the collection of the microspheres. Currently losses are incurred through particles missing the centre of the flame or falling outside of the collection trays.

Mercury intrusion porosimetry (MIP) was used to determine intraparticle porosity of the high porosity and low porosity microspheres. A challenge encountered with this technique was determining the bulk density of the microspheres from the low-pressure mercury intrusion (0.85 to 50 psia). This was due to a possible overlap of large microsphere pores (intraparticle) and the gaps/voids between different microspheres (interparticle). Consequently, SEM images were first used to determine the largest pore sizes in both microsphere samples. The bulk densities were then calculated at the mercury intrusion pressures corresponding to those SEM largest pore sizes. Intraparticle porosity was then calculated from those bulk densities. All mercury intrusion at pore sizes greater than the SEM largest pore sizes was then considered interparticulate. This still leaves the possibility for some overlap of intraparticle and interparticle pores, which could not be avoided. The cumulative volume intrusion graph in Appendix 2 Figure 3 (page: 126) also supported our approach, showing a change in gradient (point 'Y') as intraparticulate pores are filled.

Induction heating measurements (Figure 4) were undertaken to demonstrate suitability of the magnetic microspheres for CO₂ regeneration through a MISA process. An unexpected result was the almost identical heating profiles of the low and high porosity microspheres, despite their differences in composition and magnetic susceptibility determined by VSM analysis (Appendix 2 section 3.2, page: 127). The low porosity microspheres were expected to heat more rapidly due to their

higher magnetic susceptibility. The initial hypothesis was that the similar heating profiles were due to heat transfer limitations between the microspheres and the fibre optic thermocouple, due to their large spherical sizes resulting in low contact areas for heat transfer. The pristine fine and dense (unprocessed) magnetite powder (same composition as the low porosity microspheres) heated much more rapidly, supporting this hypothesis. A limitation of this method was that the measured rate of induction heating was dependant on many factors, including sample quantity, tube diameter, heat transfer etc^{119,120}. The experiments could therefore provide a useful proof of concept, and a useful comparison between samples, but the results are less useful for comparisons to other materials, compared to other characterisation methods such as VSM, measuring saturation magnetisation¹²¹.

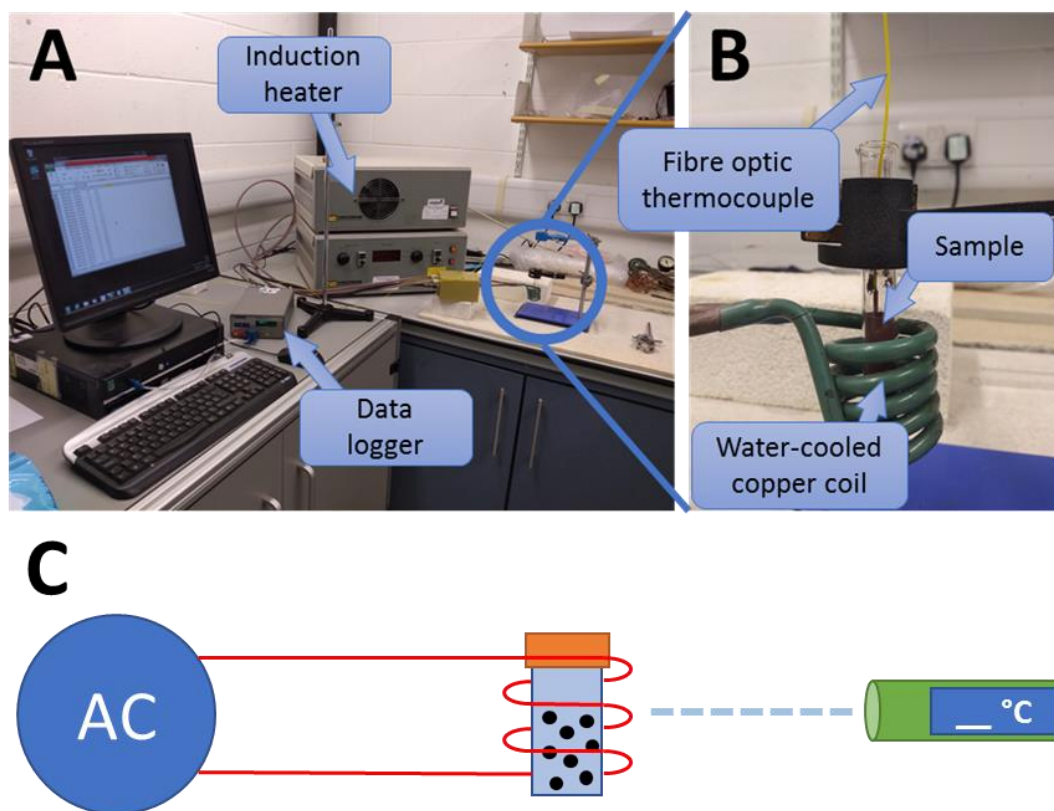


Figure 4: A: Photo of the induction heating equipment set-up, including the induction heater and data logger. B: Higher magnification photo of the sample held in the copper coil with a fibre optic thermocouple. C: Simple schematic of induction heating using an alternating current through a coil.

2.3.2 Surface functionalisation of PMMs

The high porosity PMMs were taken forward for surface functionalisation prior to MOF growth for the formation of MFCs. Several different functionalisation agents

were trialled based on previously reported MOF composite examples, including unfunctionalised¹²², PDA¹²³, PVA¹²⁴, MPYR¹²⁵, PSS¹²⁶, and MAA¹²⁷. However, it was not possible to confirm the presence of most of these on the PMMs due to the small quantities on the surfaces (<2 wt.%). As described in Appendix 2 section 3.4 (page: 133), the most effective composite formation results (highest MOF loadings) were obtained with PDA and MPYR functionalised PMMs, both of which could be identified through XPS analysis^{128–131} (page: 131). A limitation of this functionalisation approach is the method and timescales (shaker plate, overnight) required for PDA surface coating, due to the slow polymerisation of dopamine (18-24 h)^{106,132,133}. This would present challenges for the overall scalability of the method.

2.3.3 Layer-by-layer synthesis of MFCs

Once the PMMs were surface functionalised, layer-by-layer composite formation methods were used to grow MOFs HKUST-1 and SIFSIX-3-Cu on the PMM surfaces. The layer-by-layer method was chosen as it promotes heterogeneous MOF growth on the PMM surfaces, rather than homogeneous MOF synthesis in solution (detached from the PMMs). HKUST-1 and SIFSIX-3-Cu (Figure 5) were chosen due to their promise for CO₂ capture applications^{133,134}. HKUST-1 represents a well-studied archetypal framework, which is cheap to produce at scale and has shown promise for CO₂ capture applications due to its high adsorption capacity, interacting with CO₂ through unsaturated metal centres. The presence of water in the flue gas stream is known to affect the stability of the MOF¹³⁵, though with an appropriate drying step for the flue gas before CO₂ capture this could be worked around. SIFSIX-3-Cu represents a newer innovative material, which interacts with CO₂ through a kinetic/size exclusion mechanism, resulting in a very high selectivity for CO₂ and high CO₂ capacity at low partial pressures¹³³. Fe₃O₄ itself doesn't adsorb much CO₂ at standard conditions, though under high mechanical stress and pressure (30 bar) it can store CO₂ in the form of FeCO₃, which can be cycled through releasing the CO₂ again at high temperatures (300 °C)¹³⁶.

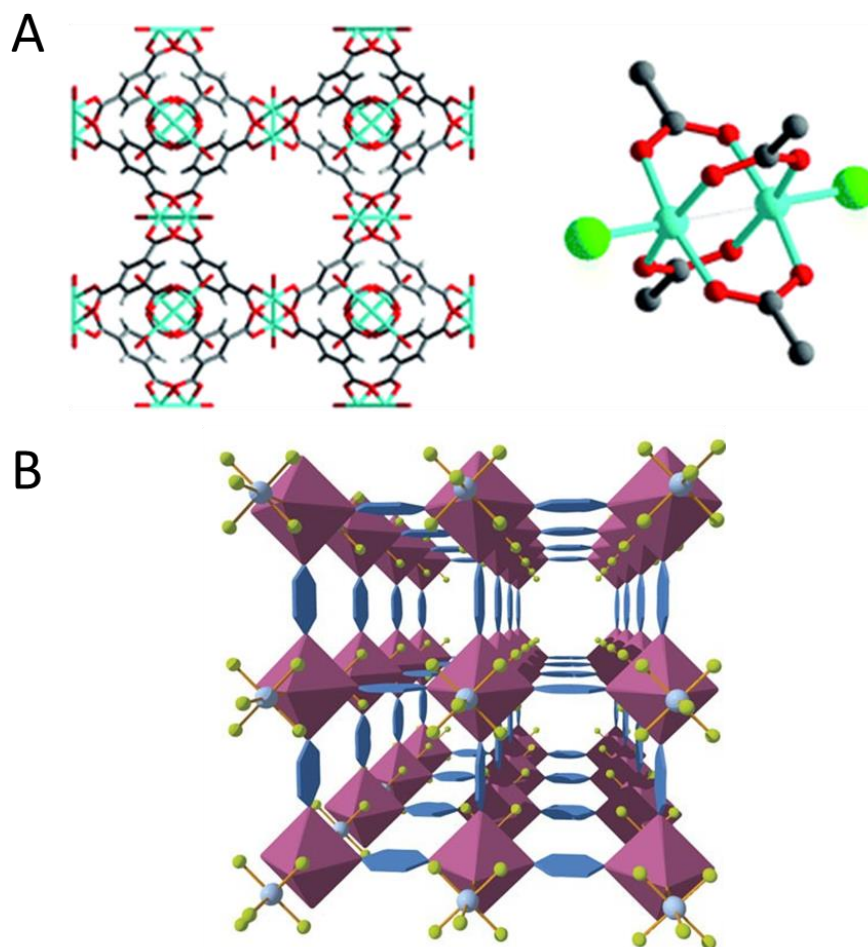


Figure 5: A: structure of MOF HKUST-1 (left), and paddlewheel secondary building unit (right) [Grey: carbon, light grey: hydrogen, red: oxygen, cyan: copper, green: exchangeable axial positions of the secondary building unit]. Figure adapted from reference⁹⁵. B: structure of MOF SIFSIX-3-Cu [blue hexagon: pyrazine, purple polyhedra: Cu, light blue: Si, light green: F]. Figure adapted from reference¹³⁴.

The main limitations of the layer-by-layer approach, as mentioned earlier in Chapter 1.3.2 (page: 11), are the many steps involved in growing the MOF (e.g. 20 cycles¹⁰⁴), and the thin MOF layers produced (<200 nm)^{102,138}. Although it is possible to automate the layer-by-layer approach¹³⁹, the scalability of the layer-by-layer synthesis is certainly more challenging than other composite formation routes such as direct or secondary growth, due to the many more steps/cycles involved. The thin MOF layers resulting from this approach may be appropriate for applications such as catalysis (e.g. biodiesel production)¹⁰⁴, where surface sites play the key role¹¹⁰. However, the low MOF layer thickness/mass fraction is limiting for applications where bulk MOF activity is required, such as gas adsorption, resulting in a low adsorption capacity per weight of MFC adsorbent. For this reason, alternative MFCs

with higher mass fractions of MOFs might be better suited for CO₂ capture applications. Ideally, a simple direct growth method could be used, and the MOF (rather than the magnetic material) would be the bulk component in the composite. This intriguing possibility led to our next investigations in the following chapters.

Chapter 3

Appendix 3 (page: 170): paper “Rapid microwave synthesis of sustainable magnetic framework composites of UTSA-16(Zn) with Fe₃O₄ nanoparticles for efficient CO₂ capture” (*Materials Advances*, 2023, 4, 5838-5849)

Key novelty:

- Scalable continuous synthesis method developed to produce highly magnetic Fe₃O₄ nanoparticles (diameter: 19 nm, saturation magnetisation: 78 emu/g)
- Fe₃O₄ nanoparticles surface functionalised with a citrate-coating in-situ
- MOF UTSA-16(Zn) synthesis optimised from 4 h (literature) to 10 min microwave method
- Novel MFCs formed via direct-growth method (yield: 81-83%) with high CO₂ adsorption capacities (2.8-3.3 mmol/g) and rapid regeneration times

3 Microwave-assisted direct growth of magnetic framework composites

3.1 Context

Chapter 1 (page: 1) first identified MFCs as a promising class of materials for energy-efficient CO₂ capture and release via magnetic induction heating. Chapter 2 (page: 14) then explored the synthesis of novel hierarchically porous MFCs via a layer-by-layer approach. Despite successfully synthesising the materials, the low mass fraction of MOF in the composites (10-11 wt.%) limited their suitability to adsorption applications due to a low adsorption capacity per weight of MFC adsorbent. In order to increase the MOF fraction in the MFCs, the approach was altered from growing MOFs on magnetic microspheres (Chapter 2, page: 14), to instead in this chapter incorporating magnetic nanoparticles within MOFs. To facilitate this new approach, a microwave-assisted (rapid and energy-efficient) direct-growth strategy was developed to grow a novel CO₂ capture MOF (UTSA-16(Zn)) around Fe₃O₄ nanoparticles.

3.2 Summary

The paper in Appendix 3 (page: 170) describes the synthesis, characterisation, and evaluation of sustainable and novel MFCs containing MOF UTSA-16(Zn) and citrate-coated Fe_3O_4 magnetic nanoparticles for post-combustion carbon-capture applications (Figure 6). Firstly, a scalable (pilot scale 80 g/h demonstrated with barium strontium titanate nanopowders¹⁴⁰) and single-step continuous hydrothermal synthesis method is detailed for the production of citrate-coated Fe_3O_4 nanoparticles (mean diameter: 19 ± 11 nm, yield: 62%). Compared to previously reported syntheses, these nanoparticles showed a very high ambient-temperature saturation magnetisation (78 emu/g) due to their high purity and crystallinity. They have suitability for a wide range of applications, particularly in biomedicine, catalysis, and environmental remediation, benefiting from ease of detection, efficient separation by magnetic fields and very rapid induction heating capability (*e.g.* for guest release). The citrate coating also offers the additional benefits of high colloidal stability, resistance to oxidation and the ability for conjugation to other molecules, useful for the formation of composites.

Secondly, innovative MFC materials were formed from the magnetic nanoparticles and pioneering CO_2 capture MOF, UTSA-16(Zn). A rapid microwave process was optimised to grow the pristine MOF (10 min, 60 °C, yield: 77%), reducing synthesis time by a factor of 24 compared to previously published studies¹⁴¹. This direct-growth method (see Table 2) was then used with the nanoparticles to produce MFCs in just 10 minutes at 81-83% yield (2.6-18.7 wt.% Fe_3O_4 in UTSA-16(Zn), *cf.* other reported MFCs: 0.1-7.8 wt% Fe_3O_4 in Mg-MOF-74¹⁴², 1-10 wt% MgFe_2O_4 in Al-fumarate¹⁴³, 1.3-7.3 wt% Fe_3O_4 in PCN-250¹⁴⁴). High CO_2 adsorption capacities (2.8-3.3 mmol/g) and recyclability were maintained, with no loss of MOF CO_2 capacity with increasing nanoparticle loading in the MFCs (no pore-blocking^{145,146}). Remarkably low regeneration temperatures were sufficient for MFC regeneration and CO_2 release (60 °C) compared to other materials (*e.g.* carbon-based materials (120-230 °C)¹⁴⁷, zeolites (200 °C)¹⁴⁸ and other MFCs (130-145 °C)¹⁷), reachable in 8 seconds via rapid magnetic induction heating.

A comprehensive range of advanced and complementary techniques were employed to characterise and evaluate the properties of the nanoparticles and MFC materials. These included: XRD and SEM/TEM with EDS to understand the structures and distributions of the composites; BET surface area and TGA CO₂ uptake analysis to measure CO₂ capture and release performance; vibrating sample magnetometry and heating under induction to evaluate magnetic properties.

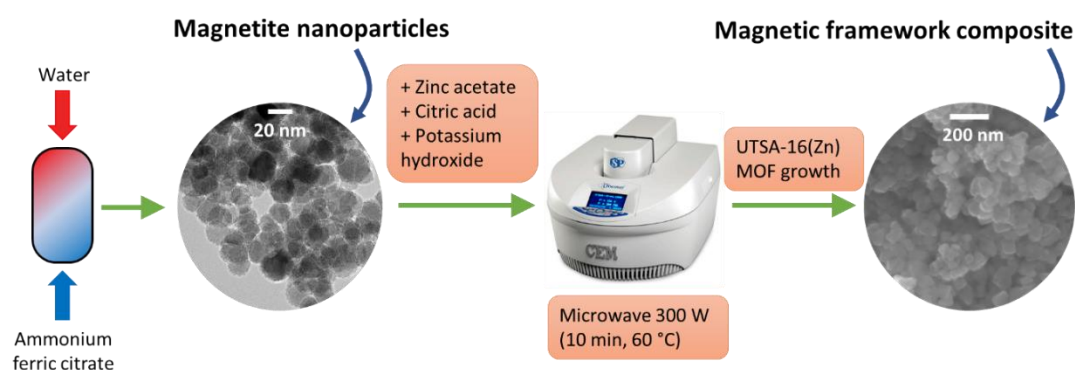


Figure 6: Schematic showing formation of magnetic framework composites from magnetite nanoparticles and MOF UTSA-16(Zn) via a microwave method.

3.3 Commentary and critical analysis

3.3.1 Magnetic nanoparticles

This study again begins with a focus on synthesising the magnetic component of the final MFC materials. Fe₃O₄ nanoparticles were selected due to the high magnetisation (218 emu/g)¹⁴⁹ and low-cost/abundance of iron compared to other elements (32.1% of the earth's mass)⁹³, as described in Chapter 1.3 (page: 8). Magnetite has often been used in the synthesis of MFCs thanks to its ease of availability and high magnetisation, exhibiting super-paramagnetism when in nanoparticle form. However, published synthesis methods commonly involved lengthy multi-step batch reactions, large volumes of organic solvents, and air sensitive environments. To overcome these limitations and improve the sustainability of the nanoparticle synthesis, a continuous-flow hydrothermal method was developed, using an inherently scalable reactor design^{150,151}. An additional aim was to surface coat the Fe₃O₄ with a citrate layer, to stabilise the nanoparticles from oxidation and aggregation, and promote binding interactions with the MOF (containing a citric acid linker) during composite formation.

The hydrothermal synthesis method successfully produced a suspension of citrate-coated Fe_3O_4 in water, though the yield could be improved (62%, calculated from the theoretical quantity of iron). However, this is not a significant limitation due to the very low cost and abundant nature of the starting material (ammonium iron citrate). The yield improved at higher temperatures (435 °C compared to 400 °C), though the maximum that could be achieved with the heating jacket on the reactor design was 435 °C. The yield may therefore be further improved with higher temperatures if a more capable heater design was implemented. Another potential constraint is that the Fe_3O_4 nanoparticles are produced in a dilute suspension (≈ 0.25 mg/mL), requiring concentration and washing to remove undesired dissolved ions. This was performed in batch at lab-scale, though a large-scale magnetic separation or continuous centrifuge and washing procedure could be utilised for process scale-up¹⁵².

Although Fe_3O_4 oxidation did not occur, magnetite is known to oxidise over time under air exposure to the less magnetic hematite ($\alpha\text{-Fe}_2\text{O}_3$) or maghemite ($\gamma\text{-Fe}_2\text{O}_3$)¹⁵³. This could then reduce the magnetisation and induction heating capabilities of the MFCs over time. To examine the influence of magnetite oxidation of the MFCs, induction heating and CO_2 capacity performance tests could be conducted over longer timescales (e.g. one year). If there is a significant negative impact on heating ability or CO_2 capacity, additional Fe_3O_4 surface protection coatings could be investigated (e.g. silica⁹⁵), or alternate magnetic nanomaterials such as MgFe_2O_4 ¹⁴².

3.3.2 Microwave-assisted direct growth of MFCs

As previously discussed in Chapter 1.3.3 (page: 11), a direct growth method of composite formation has the benefit of a low number of synthesis steps compared to alternatives. This is beneficial from scalability and sustainability perspectives, minimising material and energy loss. Another advantage is that a direct growth method usually accommodates a synthesis procedure similar or identical to the pristine MOF (in the presence of a magnetic material), and can result in the MOF becoming the majority component in the composite (e.g. ZIF-8 grown around Au/Pt nanoparticles, with only 1-4 wt.% nanoparticles in the final MFC¹⁰⁴). When choosing a

MOF for CO₂ capture applications, key desirable properties are CO₂ uptake at relevant temperatures and pressures (flue gas 40-60 °C, 0.15 bar CO₂), high selectivity for CO₂ over N₂, low regeneration energy (30-60 kJ mol⁻¹, measured by the isosteric heat of adsorption, Q_{st}), high chemical and thermal stability, and tolerance to moisture and other impurities such as SO_x and NO_x.¹⁵⁴ MOF UTSA-16(Zn) was chosen for this study due to its high performance in these metrics (especially moisture tolerance and selectivity)^{141,155}, and as the starting reagents are abundant and low-cost (<1 USD/g MOF)¹⁵⁶. This has resulted in the MOF being reviewed as a highly promising CO₂ capture material compared to other porous solids such as MOFs, Zeolites and activated carbon^{157,158}. UTSA-16(Zn) contains an anatase-type structure (Figure 7) with tetrahedral Zn(II) and octahedral Zn(II) citrate clusters¹⁵⁹. The major CO₂ binding site is the K⁺ counterions in the UTSA-16(Zn) channels. Once these are saturated (3.2 mmol/g), CO₂ then binds to a weaker adsorption site on the citrate linker¹⁶⁰ (assuming CO₂ binding similar to UTSA-16(Co)).

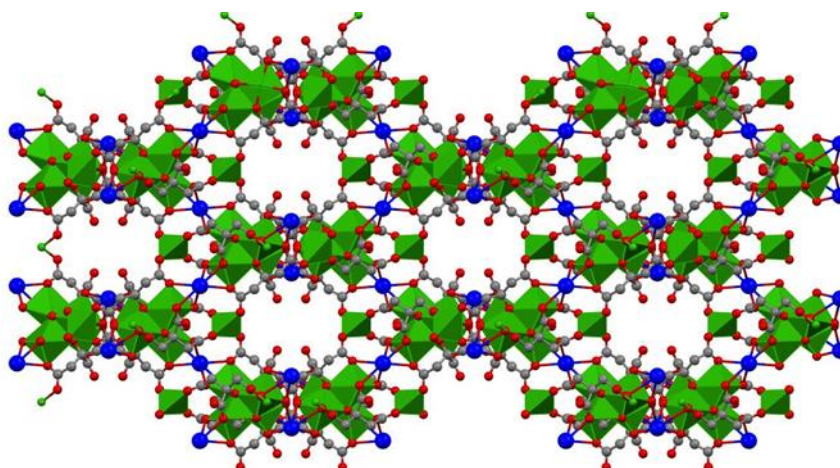


Figure 7: Structure of MOF UTSA-16(Zn) [green: Zn; blue: K, red: O, grey: C; H omitted for clarity].

The synthesis for pristine UTSA-16(Zn) described in the literature was considered challenging from scalability and sustainability standpoints¹⁴¹. The synthesis involved 4 hours microwave heating at 90 °C, followed by 14 solvent washes over 3 days using anhydrous methanol and diethyl ether, and 90 °C vacuum drying activation. In order to improve the industrial viability of UTSA-16(Zn), optimisation work was undertaken to reduce the synthesis to a 10 min, 60 °C microwave reaction, and reduce the washing and activation to 3 (non-anhydrous) methanol washes over 1 h then 50 °C drying without a vacuum (see Appendix 3 section 3.2 (page: 183) and Supplementary

Information (page: 202). Following this work, MFCs were then formulated with 3 different Fe_3O_4 concentrations in UTSA-16(Zn), to measure the impact of varying Fe_3O_4 concentrations on MFC yield, CO_2 capacity, magnetisation and induction heating capability. The overall method proved effective at producing MFCs with high CO_2 adsorption capacities (2.8-3.3 mmol/g) and rapid induction heating potential (*e.g.* reaching 60 °C in 8 s heating). An alternative method of heating via magnetic induction to form the MFCs was also considered, though since the reaction was performed in solvent with quite low concentrations of Fe_3O_4 in solution, the heating rate was considered much slower than the microwave method. However, induction heating for MFC synthesis could be considered in future, especially for solvent-free routes.

One metric investigated was the impact of regeneration temperature on CO_2 average capacity and capacity loss over repeated cycles. Particularly low regeneration temperatures (such as 50-60 °C) were sufficient for effective regeneration of the MFCs. This regeneration was performed by raising the temperature alongside switching the purge gas from CO_2 (during adsorption) to N_2 (for desorption). Despite this method's frequent use in the literature^{161–164}, demonstrating a useful proof-of-concept, a drawback of this regeneration method is that it produces a mixed N_2/CO_2 gas stream during desorption. This stream would then require further separation if pure CO_2 gas was necessary for utilisation or storage. To simplify this separation, alternative strategies include:

- Employing steam instead of N_2 for the purge gas¹⁶⁵. This would then be separated by cooling the mixed gas stream to condense out the water vapour, though would require a material with very high water stability.
- A temperature vacuum swing adsorption (TVSA) process, in which a negative pressure is applied to promote desorption at an elevated temperature²⁸. This would avoid the extra separation step entirely, though would require additional energy and equipment to apply the pressure reduction.
- Using hot pure CO_2 gas to simultaneously raise the temperature and purge the material¹⁶⁶. This would also avoid the extra separation step. However,

depending on the material, this process may decrease the working capacity due to some CO₂ adsorption at higher temperatures (*e.g.* 100 °C).

One limitation of this MFC direct growth strategy is that it is performed in batch. The fast 10-minute microwave-assisted synthesis is an improvement on lengthy solvothermal methods (*e.g.* 2 days)¹⁵⁵, but still contains scalability constraints compared to continuous flow manufacture. These include heat and mass transfer limitations due to batch vessel size and variability between individual batch repeat syntheses^{167,168}. The scales required for post-combustion CO₂ capture are huge (*e.g.* 10,000 tons for a power plant)¹⁵⁷ necessitating a process which can produce tonnes of material. For this reason, the next chapter of our research investigated the continuous flow synthesis of MOF UTSA-16(Zn) and associated MFCs using citrate-coated Fe₃O₄.

Chapter 4

Appendix 4 (page: 209): paper “Continuous flow synthesis of MOF UTSA-16(Zn), mixed-metal and magnetic composites for CO₂ capture – toward sustainable and scalable manufacture”

Key novelty:

- *First continuous flow synthesis of pioneering CO₂ capture MOF UTSA-16(Zn), optimised with record production rate (173 g/h, 77-fold increase on batch method)*
- *Mixed-metal UTSA-16(Zn,Mg) study results in 6% increase in CO₂ capacity (3.8 mmol/g at 0.018 Mg metal mole fraction)*
- *Fe₃O₄ nanoparticles incorporated in flow synthesis (3-11%) resulting in the highest production rate reported of any MFC to date (152 g/h, 12-fold increase on previous record)*

4 Continuous flow synthesis of UTSA-16(Zn), mixed-metal and magnetic composites

4.1 Context

In Chapter 1 (page: 1), MOFs were identified as promising candidates for low-energy CO₂ capture and release. MFCs containing MOFs and magnetic particles were further discussed as beneficial for overcoming the challenge of thermal CO₂ regeneration by facilitating heating *via* magnetic induction. Chapter 2 (page: 14) and Chapter 3 (page: 23) went on to explore the synthesis of various MFCs by batch methods. In particular, MFCs containing citrate-coated Fe₃O₄ nanoparticles in MOF UTSA-16(Zn) demonstrated high CO₂ adsorption capacities (2.8-3.3 mmol/g) and recyclability. These MFCs also showed remarkably low regeneration temperatures for CO₂ release compared to other materials (60 °C), which could be reached in seconds via rapid magnetic induction heating. To facilitate transition of the UTSA-16(Zn)@MNP-CA MFCs towards an industrial setting, a more sustainable and scalable manufacturing

method is required. This Chapter presents the development and investigation of such a method, using a solvothermal continuous-flow synthesis route.

4.2 Summary

The paper in Appendix 4 (page: 209) details the optimisation of a sustainable and scalable continuous-flow synthesis method for MOF UTSA-16(Zn), UTSA-16(Zn,Mg) and MFCs of citrate-coated Fe_3O_4 nanoparticles in UTSA-16(Zn). The experimental steps taken are shown in a schematic in Figure 8. Corresponding structural and chemical characterisation and CO_2 capture and release testing are also presented and discussed. A detailed optimisation study for the production of UTSA-16(Zn) identified key variables for the continuous-flow synthesis and their impacts on the product yield, CO_2 capacity, crystallinity, and particle morphology were evaluated. Chemical parameters investigated included the metal:ligand:base ratios (metal: 0.5 M, ligand: 0.4-0.6 M, base: 1.30-1.95 M) and mixed-metal syntheses with Mg incorporation (Mg metal mole fraction: 0.0-0.4). Process parameters were also explored, including the total flow rate (40-160 mL/min), ratio of the H_2O :EtOH solvent (2:1 to 1:2), and reaction temperature (25-90 °C). Justification and discussion are provided in Appendix 4 (page: 209).

To test the initial scope for scale-up, once the synthesis parameters were optimised a 10-fold increased scale experiment was performed at a production rate of 173 g/h (*cf.* batch production of UTSA-16(Zn): 2.25 g/h (Appendix 3, page: 170), and other reported MOF flow syntheses: HKUST-1 (60 g/h)¹⁶⁹, MIL-53(Al) (125 g/h)¹⁷⁰, UiO-66 (104 g/h)¹⁷¹). UTSA-16(Zn) produced in the 10-fold synthesis maintained the high CO_2 adsorption capacity (3.6 mmol/g), while the yield increased from 50% to 59%. The CO_2 capacity could be further increased from 3.6 to 3.8 mmol/g through extra post-synthesis solvent washing and soaking steps, more fully activating the MOF (additional 6 methanol washing steps and solvent exchange over 5 days). Using the optimised parameters for pristine UTSA-16(Zn) as a starting point, citrate-coated Fe_3O_4 nanoparticles were then incorporated into the flow synthesis (3-11 wt.% Fe_3O_4 ; MFC production rate: 152 g/h, previous highest 13 g/h for MgFe_2O_4 @UiO-66- NH_2 ¹⁷²) with no detrimental effect on the yield or CO_2 adsorption capacity of the MOF

component. The MFCs demonstrated rapid heating under a magnetic field (164 A/m, up to a 124 °C rise over 30 s), highly beneficial for CO₂ release and sorbent regeneration, overcoming issues with the thermally insulating nature of pristine MOFs. Regeneration times for alternative adsorbents such as activated carbon and zeolites are typically 20-40 min through conventional or microwave heating^{173,174}.

Key analysis and characterisation techniques were used to evaluate the UTSA-16(Zn) and composite products to enable purposeful optimisation. These included: TGA CO₂ gravimetric uptake to measure CO₂ capture and release performance; vibrating sample magnetometry and heating under induction to evaluate magnetic properties; inductively coupled plasma optical emission spectroscopy (ICP-OES) to determine concentrations of incorporated Mg in the mixed-metal UTSA-16(Zn,Mg) MOF; XRD and SEM with EDS to investigate crystallinity, particle morphology and Fe₃O₄ distribution in the UTSA-16(Zn)@MNP-CA MFCs.

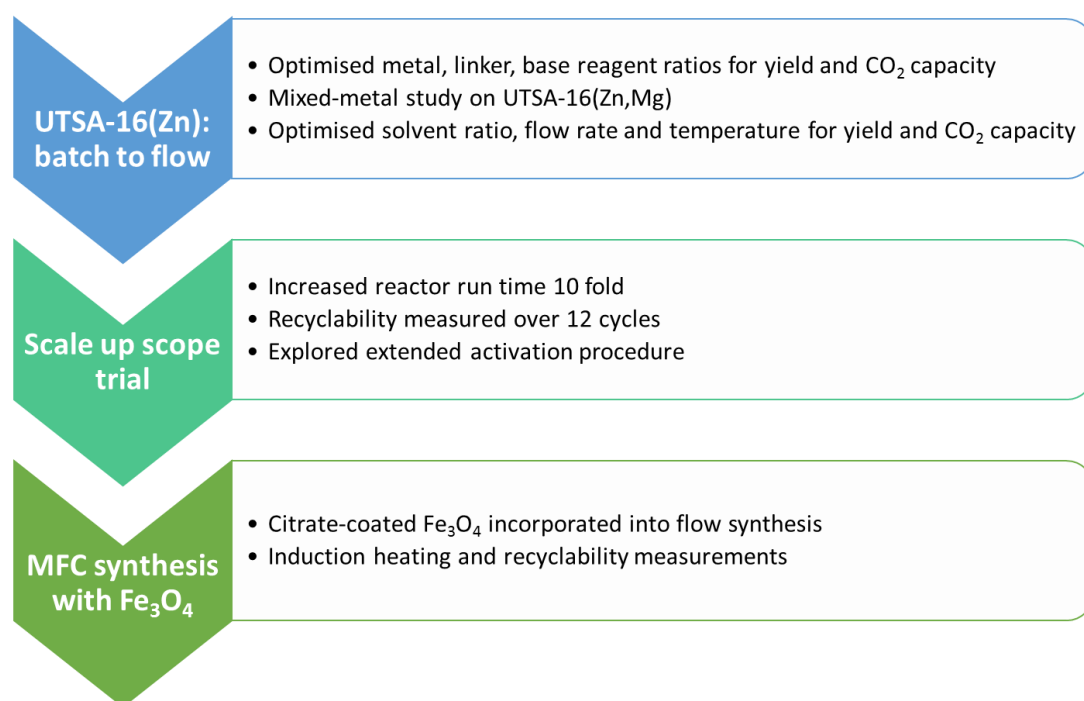


Figure 8: Schematic showing the steps taken in the optimisation of a continuous flow synthesis for UTSA-16(Zn), mixed-metal and magnetic composites.

4.3 Commentary and critical analysis

4.3.1 Parameter optimisation for UTSA-16(Zn)

A continuous flow production process was investigated for the synthesis of UTSA-16(Zn) and associated MFCs as flow synthesis offers rapid manufacture (due to high heat and mass transfer), resulting in significant improvements to production rate and space-time yield (STY)^{168,175} (e.g. HKUST-1 STY batch: $225 \text{ kg m}^{-3} \text{ d}^{-1}$, flow: $4533 \text{ kg m}^{-3} \text{ d}^{-1}$)¹⁶⁹. Other advantages of flow syntheses include improved reproducibility, lower solvent and energy consumption and reduced downtime and labour costs compared to batch syntheses^{168,175}. The study herein begins with an investigation into the impact of various chemical and process parameters on the continuous flow synthesis of UTSA-16(Zn), specifically optimising for product quality (CO_2 adsorption capacity) and yield. Corresponding XRD and SEM analyses were also used to identify crystal structures, degrees of crystallinity and morphologies, aiding understanding of structure-property relationships. As discussed in Appendix 4 section 3 (page: 218), a customised perfluoroalkoxy polymer pipe-in-pipe counter-current reactor (Figure 9) was chosen due to its simple design and rapid mixing capabilities, as previously demonstrated with a similar design for archetypal MOFs HKUST-1, ZIF-8 and CPO-27^{176,177}.

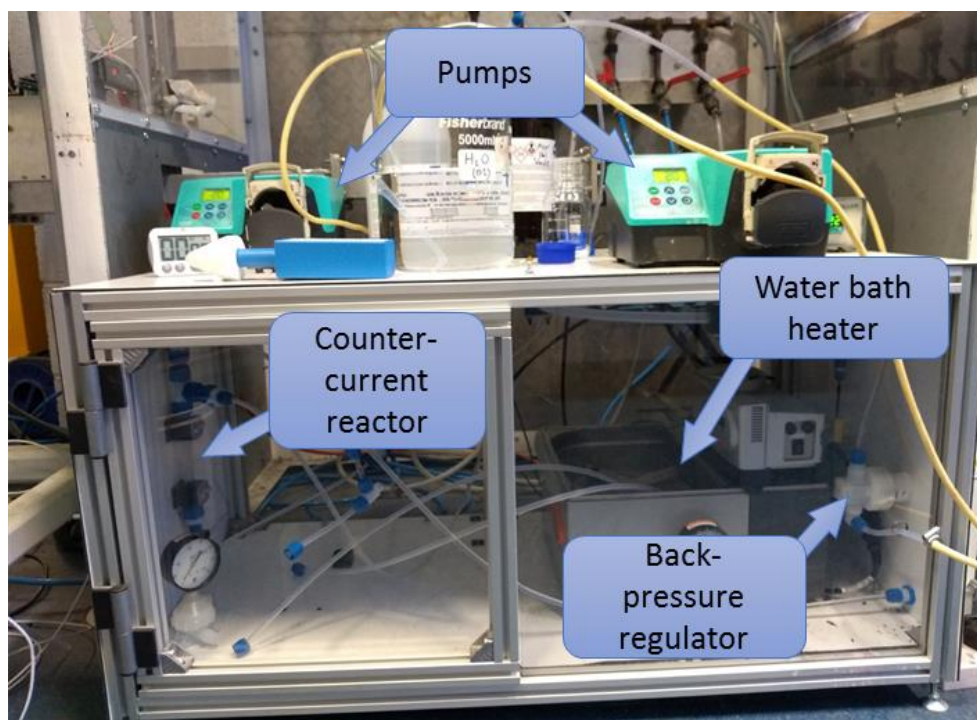


Figure 9: Photo of the general flow reactor equipment set-up, including the two pumps, counter-current reactor, water bath heater and back-pressure regulator.

A systematic approach was undertaken to adjust each variable individually. One of these investigations was into a mixed-metal UTSA-16(Zn,Mg) synthesis, as a previous study by Gaikwad *et al.* found that a 7:2 ratio of Zn:Mg in the UTSA-16 synthesis increased CO₂ capacity by 18% and CO₂/N₂ selectivity by 19% compared to pristine UTSA-16(Zn) for their method. An unexpected result of our study was the very limited incorporation of Mg into the mixed-metal UTSA-16(Zn,Mg) compared to the amount of Mg in the starting reagents (approx. 8% of added Mg was incorporated, *e.g.* 0.4 Mg metal mole fraction in reactants resulted in 0.032 Mg metal mole fraction in products). This preferential incorporation of Zn over Mg could be attributed to a number of factors, including solubility, reactivity and coordination sphere¹⁷⁸. Further discussion can be found in Appendix 4 section 3.1 (page:219). The sole reported study into UTSA-16(Zn,Mg) (by Gaikwad *et al.* via a microwave batch route) showed that 84% of Mg in the starting reagents were incorporated into the product UTSA-16(Zn,Mg), using a 7:2 weight ratio of Zn:Mg¹⁷⁹. However, this was determined by SEM/EDS mapping, which is a more qualitative technique due to the lack of standards used, and complex topographies introducing uncontrolled geometric factors which result in systematic errors (often a factor of ten or more)¹⁸⁰. Yields were not reported

by Gaikwad *et al.* The ICP-OES method used herein and described in Appendix 4 section 2.6 (page: 217) represents a more accurate methodology for determining the exact quantities of different metal ions in the mixed-metal products (identified as a best practise for MOF elemental ratio characterisation⁶⁴).

Another interesting result from our study was the alternative crystal structure observed at high base concentrations (1.95 M) and at high EtOH:H₂O solvent ratios (2:1), discussed in Appendix 4 sections 3.1 (page: 219) & 3.2 (page: 223). We theorised that this alternative structure resulted from a more rapid nucleation event (compared to a typical synthesis), caused by the high EtOH antisolvent ratio or the rapid linker deprotonation (from the high base concentration/pH). Powder XRD patterns for this alternative structure were different to the typical UTSA-16(Zn) tetragonal crystal system (space group: I-42d), and can be seen in Appendix 4 Supplementary Information (page 251), at 1.95 M KOH (aq) and 0.33 solvent fraction H₂O in ethanol. Additional peaks were present at 9, 10 and 13 °2θ, and this pattern did not match any reported structure in the diffraction database. SEM images of the alternative structure (Appendix 4 Supplementary Information, page 256) showed the presence of rod-like crystal morphologies, absent in other UTSA-16(Zn) samples. This unidentified product showed a significantly reduced CO₂ adsorption capacity (1-1.5 mmol/g *cf.* 3.6 mmol/g for the optimised synthesis for the standard UTSA-16(Zn) crystal structure), so was not further investigated.

A challenge encountered during optimisation of the flow rate was separating the variables of residence time (through the heating coil, 1-9 min) and mixing intensity (in the counter-current reactor), both of which depend on flow rate (*i.e.* a high flow rate gives a high mixing intensity but a low residence time, a low flow rate gives a low mixing intensity but a high residence time). As discussed in Appendix 4 section 3.2 (page: 223), an approach of changing flow rates after sample mixing but before the sample passed through the heating coil was adopted to separate the mixing intensity and residence time variables. The expectation was that both higher residence times and higher mixing intensities would result in higher product quality (CO₂ capacity) and % yield, due to improved mass transfer from faster mixing and improved heat transfer from the longer residence times^{181,182}. However, an unexpected result was

that higher flow rates/mixing intensity through the reactor (*e.g.* 160 mL/min) were not always beneficial to product quality (CO₂ capacity), even with a high residence time, and that optimal mixing efficiency (resulting in maximum CO₂ adsorption capacity) was at 80 mL/min. Mixing regimes are therefore likely to be important in the flow synthesis of UTSA-16(Zn), and would need to be carefully considered on transfer to larger scale flow rigs.

A limitation faced when optimising the coil heater temperature was the boiling point of the solvent mixture. Higher temperatures benefited both CO₂ adsorption capacity and product yield (CO₂ capacity: 3.4 mmol/g (70 °C), 3.6 mmol/g (85 °C); yield: 45% (70 °C), 63% (85 °C)). However, the 1:1 EtOH:H₂O solvent mixture started to boil in the tubing at around 85 °C, resulting in an uneven flow rate. A back pressure regulator was employed to prevent boil off, although the pumps struggled to maintain a consistent flow rate against the back-pressure at 90 °C. More powerful peristaltic pumps could be tested to see if they could better maintain flow rates against the back-pressure.

The quality of UTSA-16(Zn) synthesised here showed a slight improvement compared to that made in the 10 min microwave batch method in terms of CO₂ adsorption capacity (3.6 mmol/g in flow, 3.4 mmol/g in batch), though the yield was lower due to the short residence time (50% in flow, 75% in batch). Crystallinity by X-ray diffraction was similar from both methods.

4.3.2 Scale-up and production of MFCs

Continuous-flow syntheses can be scaled up in several ways. This includes extending the run time for a synthesis, parallelisation, or increasing the size/flow rate of the reactor. As a test of the simplest scale-up method (extending the run time), a larger scale batch of UTSA-16(Zn) was synthesised by extending the run time of the flow rig (2.5 min, 10 g scale) 10-fold compared to the duration of the optimisation batches (15 s, 1 g scale). CO₂ adsorption capacity was maintained at 3.6 mmol/g, and the yield increased from 50% to 59% due to a reduction of losses during product collection (less proportion of material left in the tubing). A production rate of 173 g/h was achieved for the 10 g scale synthesis on the lab-scale rig at a flow rate of 80

mL/min. The space-time yield (STY) was calculated at 23,573 kg m⁻³ d⁻¹, *cf.* batch production of UTSA-16(Zn) in Appendix 3 (page 170): 1543 kg m⁻³ d⁻¹ and other MOF flow syntheses¹⁸³: HKUST-1 (4533 kg m⁻³ d⁻¹), MIL-53(Al) (1300 kg m⁻³ d⁻¹), UiO-66 (672 kg m⁻³ d⁻¹). However, this metric is considered less representative for comparing MOF flow syntheses, as STYs are prone to over-extrapolation and have high variation based on how the reactor or reaction mixture volume is calculated^{184,185}. Both the production rate and STY were comparably very high for MOF flow syntheses, as discussed in Appendix 4 section 3.3 (page: 227). Additional washing and solvent soaking steps (further 6 methanol washing steps with solvent exchange over 5 days, on top of standard procedure of 3 methanol washes over 1 hour) resulted in a 6% increase (from 3.6 to 3.8 mmol/g) in CO₂ adsorption capacity of UTSA-16(Zn), but at the significant expense of additional solvent use, time and energy. Downstream processing of MOFs is already a significant material, time and energy cost⁶³, making the slight increase in CO₂ capacity with extra activation steps unlikely to be favourable from an industrial scale standpoint.

Multiple quantities of citrate-coated Fe₃O₄ (0.5-2 mL, 5% aq. solution) were then added to the dissolved MOF precursor solutions before pumping, forming UTSA-16(Zn)@MNP-CA MFCs upon mixing with EtOH in the counter-current reactor and heating in the coil heater (CO₂ capacity: 3.1-3.5 mmol/g, yield: 49-52%). The product yield was unaffected by MFC formation (*cf.* 50% without Fe₃O₄), unlike the microwave batch synthesis of UTSA-16(Zn)@MNP-CA (Appendix 3 section 3.2, page: 183), where the incorporation of Fe₃O₄ benefited the yield. This benefit was possibly due to higher localised temperatures around the Fe₃O₄ nanoparticles from enhanced interactions with the microwave field^{186,187}. The addition of Fe₃O₄ also had no detrimental impact on the CO₂ capacity of the UTSA-16(Zn) MOF component (3.6 mmol/g). A limitation of this approach was that the Fe₃O₄ magnetic nanoparticles were synthesised separately (albeit also *via* a continuous-flow method) before MFC synthesis, due to the differing reaction conditions (Fe₃O₄: 435 °C, H₂O, 24 MPa; UTSA-16(Zn): 80 °C, EtOH:H₂O 1:1, 0.1 MPa). A further improvement to the sustainability of the process could be achieved if the two flow reactions could be done in a telescoped fashion¹⁶⁸, with the Fe₃O₄ flow synthesis product flowing into the MFC

flow synthesis (saving time and labour costs, also potentially reducing solvent usage¹⁸⁸). An alternative option could be to investigate whether the nanoparticles could be synthesised simultaneously with the MOF to form the MFC in a single flow reactor, though this would likely be challenging with Fe_3O_4 and UTSA-16(Zn) specifically due to the highly different reaction conditions.

A limitation of our analysis was that as we had no access to actual or simulated flue gas, we were unable to test the materials under those conditions. Studies in the literature have shown the promise of UTSA-16(Zn) due to its high stability to water and NO_x , though it does start to lose its CO_2 capacity after exposure to SO_x ¹⁴¹. Nevertheless, testing of the MFCs under realistic flue gas conditions would be highly desirable in future.

CO_2 adsorption capacity was measured and recorded in mmol/g for these MFCs and indeed all materials produced in this thesis. This is the standard procedure for comparing different materials in the literature, however, since packed beds would be used for storing the materials in industrial CO_2 capture applications, discussion on volumetric capacity is equally important. This would require first shaping the MOF/MFC powders into pellets or granules, then measuring their packing density to get a useful value for realistic volumetric CO_2 capacity.

Chapter 5

5 Conclusions and future work

5.1 Overall conclusions

The attached manuscripts in Appendices 2-4 present a coherent body of work to advance magnetic framework composites toward CO₂ capture applications. Both porous microspheres (Appendix 2, page: 109) and coated nanoparticles (Appendix 3, page: 170 & Appendix 4, page: 209) were explored as magnetic components. MOFs HKUST-1, SIFSIX-3-Cu (Appendix 2) and UTSA-16(Zn)/UTSA-16(Zn,Mg) (Appendix 3 & Appendix 4) were studied as the framework components. Various synthetic routes were investigated including layer-by-layer batch (Appendix 2), direct growth microwave-assisted batch (Appendix 3) and direct growth by continuous flow (Appendix 4) to form the composites. The MFC products were comprehensively characterised (revealing structure-property relationships) and analysed for CO₂ capture and release performance.

Key conclusions are summarised as follows:

- A rapid flame-spheroidisation process can be utilised to produce highly macro-porous (intraparticle porosity: 95%, pore diameter: 12.4±13.4 µm) iron/calcium oxide magnetic microspheres (206 ± 38 µm), suitable as a single-material porous magnetic scaffold for the synthesis of hierarchically porous MFCs when combined with micro or meso-porous materials.
- These porous magnetic microspheres can be surface functionalised with polymer and self-assembled monolayer coatings (shown with 0.7-1.2 wt.% PDA and MPYR) to facilitate the formation of MFCs. This was demonstrated *via* a layer-by-layer synthesis method with MOFs HKUST-1 (10 wt.% loading) and SIFSIX-3-Cu (11 wt.% loading). The tailored procedure of further functionalising the PDA surface with MPYR (matching the functionality of the MOF linker) improved MOF loading for SIFSIX-3-Cu from 8 to 11 wt.%.

- A scalable single-step continuous-flow hydrothermal method can be used to produce highly magnetic (saturation magnetisation: 78 emu/g) citrate-coated Fe₃O₄ nanoparticles (19 ± 11 nm), avoiding the need for harsh and lengthy batch synthesis conditions and additional functionalisation steps.
- Various concentrations of these magnetic nanoparticles can be embedded into MOFs *via* a microwave-assisted direct growth strategy, demonstrated with MOF UTSA-16(Zn) (3-19 wt.% nanoparticles incorporation). The resulting MFCs maintained high CO₂ adsorption capacities (2.8-3.3 mmol/g) and recyclability, without loss of MOF CO₂ capacity with nanoparticle incorporation. Regeneration temperature impacted total CO₂ capacity and capacity loss over multiple cycles. Remarkably low temperatures (60 °C) were enough to regenerate the MFCs compared to other solid adsorbents, which could be achieved in 8 seconds *via* magnetic induction heating, overcoming the challenge of rapid and low energy thermal regeneration in CO₂ capture applications.
- A continuous-flow solvothermal method can increase the production rate of UTSA-16(Zn) from 2.25 g/h (batch) to 173 g/h (flow), greatly aiding the transition of this MOF toward industrial application. A metal:linker:base ratio of 1:1:3, a 1:1 H₂O:EtOH solvent ratio, 80 mL/min flow rate and a 80 °C water bath temperature result in an optimal CO₂ adsorption capacity of 3.6 mmol/g and a MOF yield of 50%. Higher temperatures improve both yield and CO₂ capacity, but require a back-pressure regulator to prevent solvent boiling. Magnesium can be incorporated into the UTSA-16(Zn) structure, improving the CO₂ adsorption (3.8 mmol/g at 0.018 Mg metal mole fraction in product), though only ≈8% of the added Mg was incorporated, resulting in losses to the yield (35%). Scaling up by increasing the run time (10-fold) had no negative impact on CO₂ capacity and increased the yield to 59%, and additional solvent washing steps showed that CO₂ capacity could be improved (3.8 mmol/g) at the expense of the reaction sustainability.
- Citrate-coated Fe₃O₄ nanoparticles can be incorporated into the flow synthesis for UTSA-16(Zn) with no detrimental impact on yield or CO₂

capacity of the MOF component. The resulting MFCs contained 3-11 wt.% nanoparticles and demonstrated the highest production rate of any MFC to date (152 g/h), demonstrating the scalability of this novel class of materials. The flow method developed will facilitate the transfer of UTSA-16(Zn) and corresponding MFCs syntheses to pilot-scale reactors, enabling their testing in CO₂ capture application environments.

- The low-cost and sustainable methods developed in this thesis will also support the discovery, understanding and scale-up of other MOFs and MFCs, encouraging their transition to larger scale synthesis and facilitating their use for a broad range of industrial applications.

5.2 Future work

As demonstrated in this thesis, MFCs show great potential for CO₂ capture applications due to their high capacities and selectivities for CO₂, coupled with low-energy regeneration for reuse by magnetic induction heating. However, their transition to industry is limited by small lab-scale syntheses and lack of realistic/scaled application environment testing (*e.g.* packed or fluidised bed of MFC pellets in an induction coil rig). The next stage of this research must address these limitations by developing a holistic magnetic-induction low-energy CO₂ capture and release system. This would first require a more fundamental understanding of MFC nucleation and crystallisation in sustainable flow synthesis reactors, which would facilitate the effective transition to larger scale reactors ($\geq$ kg scale). Following that, the development of shaped MFC pellets would be required for use in packed or fluidised bed adsorption columns. This would also unlock new avenues of research and applications for these materials, such as in the capture or separation of other pollutant gases and environmental contaminants^{189,190}. Finally, these pellets could then be tested in a magnetic-induction adsorption rig.

5.2.1 Manufacture MFCs through large-scale continuous-flow reactors

The work described in Chapter 4 (page: 30) and Appendix 4 (page: 209) have shown that transition from a small batch synthesis to a flow reactor is possible for an MFC,

but the yield is low (50%). Further advancements could be made to the process through:

- Exploring the core science of MFC UTSA-16(Zn)@MNP-CA nucleation and crystal growth with a range of flow reactors (including at elevated temperatures and pressures) through inline and *ex situ* characterisation methods (Raman, small angle X-ray scattering, X-ray absorption fine structure spectroscopy, X-ray diffraction), understanding structure-property relationships and reaction kinetics and thermodynamics to improve synthesis yield and material quality (gravimetric and volumetric CO₂ capacity).
- Testing MFC flow syntheses with different UTSA-16(Zn) mixed-metal MOFs, alternative MOFs for CO₂ capture (*e.g.* HKUST-1, MOF-5, UiO-66) or MOFs for alternative applications (*e.g.* MIL-100(Fe), ZIF-8) to explore the applicability of the synthesis approach to other materials.
- Examining the influence of magnetite oxidation on MNP-CA and MFC magnetisation and induction heating capabilities, and if needed exploring other coatings for Fe₃O₄ or different magnetic nanoparticles entirely (*e.g.* MgFe₂O₄) to avoid any potential negative impacts of Fe₃O₄ oxidation.
- Assessing the viability of joining the continuous flow syntheses of the MNPs and MOFs to form MFCs in a single telescoped process, or alternatively forming the MNPs simultaneously with the MOF in a single step, reducing solvent usage, time and labour costs.
- Exploiting the knowledge developed to enable tech-transfer to larger pilot-scale flow reactors, demonstrating industrial scale viability.
- Investigating alternative scalable synthesis reactors for MFCs, such as a large microwave-assisted batch reactors or continuous stirred-tank reactors, comparing results with current flow reactors.
- Optimising MFC activation procedures to maximise both CO₂ capacity and sustainability.

5.2.2 Shape MFCs into pellets with advanced characterisation

Industrial application of MFCs (e.g. for CO₂ capture) would require shaped pellet formulations for use in packed-bed adsorption columns. This could be investigated through:

- Synthesising MFC pellets using various binder formulations, such as polyvinyl alcohol, polyvinyl butyral or polyvinyl pyrrolidone. Binderless pressure compaction could also be considered, as well as dry powder binders such as bentonite, lignins or sorbitols.
- Testing the pellets for key performance indicators, such as magnetisation, thermal diffusivity/conductivity, heat capacity and mechanical stability. The results could then be benchmarked against the current best alternatives, including porous carbons and zeolites.

5.2.3 Build a magnetic-induction adsorption rig for application testing

Once the MFC flow synthesis has been improved and scaled up, and MFC powders have been processed into pellets, the next step would be to test these in a magnetic-induction adsorption rig, demonstrating the viability of MFCs for industrial application. This would require:

- Designing and modelling (computational fluid dynamics) a packed-bed adsorption rig with rotameters, CO₂ detectors and an induction coil for MFC regeneration and re-use.
- Building the adsorption rig and testing different MFC pellet formulations for CO₂ capture and release performance, identifying the most promising candidates.
- Testing pellets by breakthrough analysis in low and high humidity environments with model flue gas mixtures to explore their stability in realistic application environments.
- Exploring regeneration methods which don't result in a mixed N₂/CO₂ gas stream during desorption, such as using steam, hot CO₂ or a TVSA process, facilitating the separation of pure CO₂ for storage or further utilisation.

- Performing a life-cycle assessment (LCA) and techno-economic analysis (TEA) on the magnetic-induction CO₂ capture and release system, considering cost of materials, activation and regeneration over product lifetimes. The system could then be analysed for environmental impact, re-designing where appropriate (according to the results), and comparing to alternative CO₂ capture systems in terms of cost per kilogram of captured CO₂⁵³.

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Appendix 1

Evaluating the purification and activation of metal-organic frameworks from a technical and circular economy perspective

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Statement of contribution

- Woodliffe J. L.: literature review/research, creation of figures/tables, writing original draft, review & editing, topic conceptualisation
- Ferrari B.: review & editing
- Ahmed I.: review & editing
- Laybourn A: review & editing, topic conceptualisation

Manuscript:

Evaluating the purification and activation of metal-organic frameworks from a technical and circular economy perspective

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Abstract

Metal-organic frameworks (MOFs) are highly porous materials consisting of metal ions or clusters linked by organic molecules. The high value of MOFs arises from the amount of empty space within their structure (up to 90%) and their tuneable structures and functionalities. To take full advantage of their porosity, MOFs must first be purified and activated whereby pore blocking agents present after synthesis are removed from the pores of the MOF thus exposing their high internal surface areas. Purification and activation can be challenging from both a technical perspective, due to possible framework collapse, and a sustainability perspective, due to high energy and resource demands. The circular economy model aims to eliminate waste and avoid continual use of finite resources whilst balancing considerations of society, the economy, and the environment. Its application to the chemical industry has resulted in the field of sustainable chemistry which focuses on the design, manufacture, and use of efficient and more environmentally benign chemical products and processes. In this contribution we critically evaluate the technical benefits and challenges of current MOF purification and activation methods, including against principles from the circular economy model, focusing on considerations for scalability, waste reduction, material reuse, and energy efficiency. We also discuss how a circular economy approach could inform the design and manufacture of future economically and environmentally sustainable MOF

purification and activation processes which are key to realising the immense opportunities offered by these materials.

Abbreviations

BDC	1,4-Benzenedicarboxylate
BET	Brunauer-Emmett-Teller
bipy	2,2'-Bipyridine
btb	Benzene-1,3,5-tribenzoate
BTC	1,3,5-benzenetricarboxylate
CAPEX	Capital expenditure
COF	Covalent-organic framework
CVB	4-(2-carboxyvinyl)benzoate
DCM	Dichloromethane
DEF	<i>N,N</i> -Diethylformamide
dhtp	6,6'-Dihydroxy terpyridine
DMA	<i>N,N</i> -Dimethylacetamide
DMF	<i>N,N</i> -Dimethylformamide
DMSO	Dimethyl sulfoxide
DOT	2,5-Dioxidoterephthalate
DUT	Dresden University of Technology
FIR	Fujian Institute of Research
FJI	Fujian Institute
FT-IR	Fourier-transform infrared spectroscopy
fum	Fumarate
HCl	Hydrochloric acid

HKUST	Hong Kong University of Science and Technology
IRMOF	Isorecticular metal-organic framework
MFC	Magnetic framework composite
MFM	Manchester Framework Material
MIL	Materials of Institut Lavoisier
mIM	2-Methylimidazolate
MISA	Magnetic induction swing adsorption
MOF	Metal-organic framework
NDC	2,6-Naphthalenedicarboxylate
NMR	Nuclear magnetic resonance
NOTT	Nottingham (University of)
NU	Northwestern University
OPEX	Operational expenditure
PCN	Porous coordination network
PFA	Perfluoroalkoxy
PXRD	Powder X-ray diffraction
SCD	Supercritical carbon dioxide
SNU	Seoul National University
TBAPy(H ₄)	1,3,6,8-tetrakis(<i>p</i> -benzoicacid)pyrene
TC-TTF	Tetra(carboxyl)tetrathiafulvalene
TCPP(H ₂)	Tetrakis(4-carboxyphenyl)porphyrin
TGA	Thermogravimetric analysis

THF	Tetrahydrofuran
TPDC	<i>p</i> -Terphenyl-4,4''-dicarboxylate
UiO	Universitetet i Oslo
UMCM	University of Michigan crystalline material
US	Ultrasound
UV-Vis	Ultraviolet-Visible
UVA	Ultraviolet A
WCED	World Commission on Environment and Development
XRD	X-ray diffraction
ZIF	Zeolitic imidazolate framework

1 Introduction

Metal-organic frameworks (MOFs) are a class of porous coordination polymers consisting of metal ions or clusters as nodes and organic molecules as linkers.¹ As a result of their tuneable nature and high internal surface areas, MOFs have been proposed for wide-ranging energy and environmental applications such as in selective gas adsorption and separation,² hydrogen storage,³ fuel cells,⁴ artificial photosynthesis and solar energy conversion,⁵ as chemical sensors,⁶ catalysis,⁷ drug delivery and biomedicine,⁸ and more.⁹ Some MOFs have now emerged onto the commercial market via BASF¹⁰ and university spin out companies producing industrially relevant quantities¹¹ and with products in areas such as toxic gas storage, food preservation, and antimicrobial coatings.¹² Although MOF synthesis techniques have been well reviewed in the literature,^{13,14} and scalability and sustainability assessments have been made,^{15,16} the final key steps in producing MOFs with permanent porosity, purification and activation, are often overlooked.

During purification and activation the important high surface area is made available by removing pore blocking agents (*e.g.* solvent or other chemicals, such as modulators, used during the synthesis) from the pores of the framework.¹⁷ This has traditionally been challenging, as during activation the structural integrity of the MOF can be compromised and framework collapse can occur, resulting in a loss of porosity and ultimately a drastic reduction in the usefulness of the material.¹⁷ Although significant progress has been made in overcoming pore collapse for established activation procedures such as solvent exchange, supercritical carbon dioxide processing, and freeze drying, exemplified by successful activation of several frameworks,^{18–20} their contribution towards the sustainability and scalability of overall MOF production is largely neglected. These routes typically involve significant energy and solvent consumption. Recently technologies such as microwave heating, UV-Vis irradiation, and ultrasound treatment have been explored for MOF purification and activation.^{21–23} Though these routes offer improved energy efficiency, further optimisation is needed in order to realise an environmentally and economically sustainable MOF production route required by industry.

The circular economy is a topical economics model aimed towards sustainable development.²⁴ It seeks to balance considerations of society, the economy and the environment through principles such as waste prevention and life cycle assessment. Its application to the chemical industry has led to the development of the field of sustainable and circular chemistry and chemical engineering, where resource and energy efficiency are key factors when evaluating research at all levels.²⁵ Improving the scalability and sustainability of MOF purification and activation techniques by applying principles of the circular economy would significantly contribute towards industrial scale production of MOFs, allowing their property benefits to reach real-world applications. Opportunities for circular processing such as the reuse of chemicals used in the purification and activation steps would hugely benefit large-scale production, reducing cost, waste, and environmental impact.

In this perspective we critically review the current state of the art in MOF purification and activation techniques by comparing their technical benefits and challenges against principles from the circular economy model and ‘twelve principles of circular chemistry’.²⁵ Considerations for scalability, waste reduction, material reuse, and energy efficiency are also evaluated. Importantly, we discuss how a circular economy model may inform the design of prospective MOF purification and activation processes. This paper is not intended to be an exhaustive review of the literature, but instead will highlight considerations for some of the most important advances in MOF purification and activation to date. As such, this review will serve as a guide for progressing this area by identifying future research and development opportunities.

2 The Circular Economy and MOFs

2.1 Background

Sustainability, as defined by the World Commission on Environment and Development (WCED), is “Development that meets the needs of the present without compromising the ability of future generations to meet their needs”.²⁶ Moreover, sustainable development aims at striking a balance between economic development,

environmental impact, and societal equity – the triple bottom line developed by Elkington in 1998.²⁷

The circular economy is an economic system aimed at sustainability, developing the economy without the depletion of finite natural resources.²⁴ The concept is often first attributed to Pearce and Turner in their work on the economics of natural resources and the environment in 1991.²⁸ It can broadly be defined as an economic system which replaces the linear ‘make-use-dispose’ concept with that of reducing, reusing, and recycling materials through the production, distribution, and consumption processes, decoupling the consumption of resources from economic growth.²⁴ The European Waste Framework Directive (2008/98/EC)²⁹ provides a useful waste hierarchy and definitions of terms, and the European Commission’s Circular Economy Package³⁰ offers a helpful look at some practical applications. A consideration of the application of these initial principles in the life cycle of MOFs is given below:

- Reduction in industry is implemented through minimising the amount of energy and raw materials used, and minimising waste or emissions generated.³¹ In the context of MOFs, the reduction principle could involve more resource efficient synthesis, purification and activation routes, such as reduced solvent or solvent free methods,^{32,33} (noting that some solvent free methods are typically energy intensive), reduced duration of these processes, or higher yields and conversion efficiencies. Waste can be further reduced by considering and minimising the toxicity of reagents used throughout MOF production. By-products generated during production would then have greater potential for reuse within the production process or in alternative processes. For methods which involve heating, energy requirements could be reduced by more efficient heating during synthesis and/or purification and activation, such as by microwave or induction methods.^{34,35}
- Reuse has been shown to be less demanding on the environment, requiring fewer resources, less energy and less labour when compared with the manufacturing of a product from virgin materials, recycling or disposing.³⁶

With respect to MOFs, the reuse principle could be applied by collecting the solvent and unreacted starting materials from synthesis, purification, and activation, using them again for the next batch. However, the level of purity and associated costs must also be considered. For end applications, the MOF structures need to be stable and able to be regenerated over multiple cycles whilst still retaining their key functional properties, either *in situ* or externally,³⁷ which can be designed in the synthesis stage.

- Recycling, although clearly reduces the amount of waste sent for disposal, also carries the risk of taking emphasis away from the more impactful principles of reduction and reuse. Recycling is less sustainable than reducing or reusing in terms of resource efficiency and profitability, being limited by material complexity.^{38,39} In MOF use, this principle may be applied when reuse is not feasible. If the spent MOF, waste solvent, or unreacted starting materials can't be collected for reuse, they may still be recycled for use in other applications, *e.g.* MOF-derived materials for electrochemical energy storage and conversion.⁴⁰ The geometry of manufactured MOF products and the selection of amenable binders will aid the separation and recycling processes.^{41,42}

2.2 Further Applications

Additional principles for a circular economy have been highlighted in a report by the Ellen MacArthur Foundation in 2014.⁴³ Firstly, products should be designed and optimised for a cycle of disassembly and reuse. This would design out waste and reduce energy and labour loss. For example, MOFs could be designed at the synthesis stage to have high reusability in their end applications, and to be easily broken down into constituent parts at end-of-life. Secondly, it was noted that a differentiation should be made between the consumable and the durable components of a product. Consumable components should be largely biological (defined by the Ellen MacArthur Foundation as materials that can safely re-enter the natural world)⁴⁴ and non-toxic, and able to be returned to the biosphere after use. Durable components are those which cannot biodegrade, such as metals or plastics, and should be designed for reuse or upgrade. MOFs would fit the 'durable components' category

and so should be designed for reuse or upgrade, for example, by post-synthetic modification.⁴⁵ Thirdly, it was emphasised that the energy used in powering this cycle should be entirely renewable; this would not only decrease the dependence on finite resources, but also increase systems resilience.⁴³ Efforts should be made to minimise energy use and maximise efficiency in MOF life cycles.

Using the concept of the circular economy and taking into account the triple bottom line of sustainable development, researchers at the University of Amsterdam re-evaluated the twelve principles of green chemistry⁴⁶ into an analogous twelve principles for 'circular chemistry'.²⁵ These help assess the sustainability of a chemical process, enabling the transition from a linear to a circular economy model in the chemical industry. They shifted the focus from 'green' chemistry to 'sustainable' chemistry, using life-cycle and circularity thinking to renovate the field.^{25,47} These principles have been used in this work to assess the opportunities for circularity and increased sustainability in the life cycle of MOFs, as shown in Figure 1. Similar principles have already been used to assess other products and feedstocks, such as food waste in a biorefinery,⁴⁸ insulation materials in the construction industry⁴⁹ and also elsewhere in the chemical industry⁵⁰ in order to shift from linear to circular economy models.

Throughout the whole MOF life cycle in Figure 1, the principle of reduction is applied in designing for maximum resource conversion and process and energy efficiencies, with no chemical toxicity released into the environment. The 'Resource Hierarchy' is also shown in Figure 1, which is highlighted by Keijer *et al.* to assess the end-of-life options for a product.²⁵ Higher options on the ladder are more favourable and should be implemented more frequently than lower options. It is also emphasised that service-based business models should be adopted, which shift ownership back to the producer encouraging efficiency and durability over production rate and quantity. This approach would help promote the manufacture of MOFs with long service lives and higher resource efficiencies. The regeneration stage in Figure 1. shows the collection of captured molecules for alternative uses; this would be dependent on the application of the MOF and what molecules have been captured. For example, in

the use of MOFs for post-combustion carbon capture, the captured CO₂ could be collected upon regeneration and used as a chemical feedstock.⁵¹

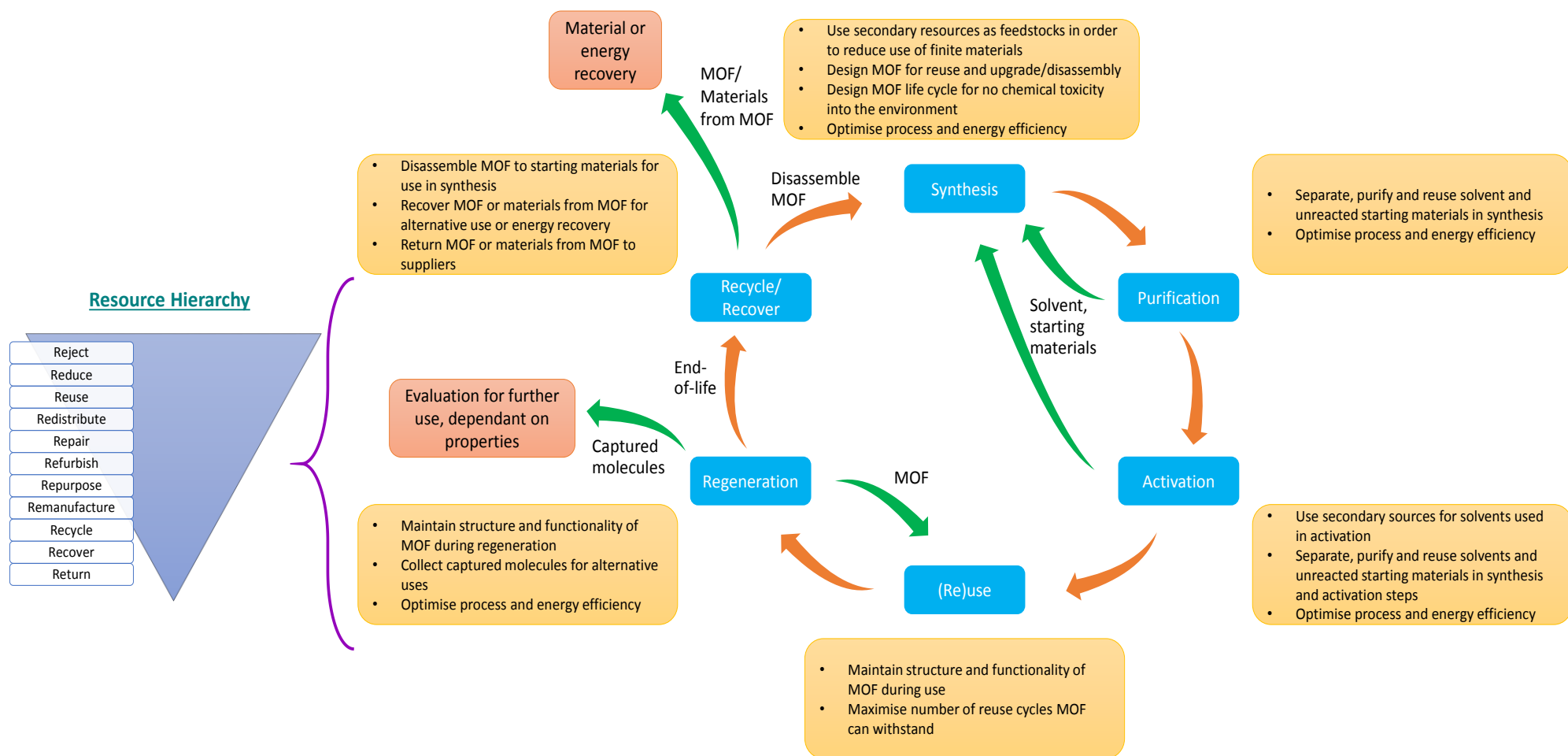


Figure 1: A representation of circular and sustainable opportunities in a MOF life cycle, applying principles of 'circular chemistry' including the 'Resource Hierarchy' ladder²³

3 MOF Purification and Activation Techniques

Significant progress has been made in developing energy and resource efficient methods for MOF synthesis.^{15,16} However, less information can be found about the sustainability of other areas in a MOF life cycle. Purification and activation are major steps in the overall MOF production process and can often be resource, energy, and time intensive. Indeed, the high costs of downstream processing (which may be greater than the reaction steps) in many chemical processes are frequently overlooked, and this is also the case for MOFs. This section of the review focuses on the state of the art in MOF purification and activation techniques, providing a technical comparison and an assessment from sustainability and scalability perspectives. Further opportunities for improving the sustainability of other areas of a MOF life cycle are also shown in Figure 1.

The terms ‘purification’ and ‘activation’ are sometimes used interchangeably in the literature. In this review, ‘purification’ refers to removal of any unreacted or decomposed reactants or other chemicals from within the MOF structure, which can then be followed by a final activation step. ‘Activation’ refers to complete removal of pore blocking agents, leaving an empty framework. The whole process (purification and activation) can involve single or multiple stages.

Purification and activation are typically the final steps in MOF production and most often involve the removal of encapsulated solvents or unreacted organic linkers from within the framework to yield a MOF with high internal surface area and permanent porosity.⁵² Often surface areas and pore volumes observed experimentally are lower than those predicted by simulations, and this is usually attributed to incomplete purification and activation or framework collapse.^{17,53} Although experimentally achieved surface areas are not a requisite of theoretical values, simulations do provide a guideline as to how much room for improvement there is in the purification and activation of a particular MOF.⁵⁴ A challenge for the activation step is to find a process which does not cause structural collapse of the MOF, resulting in a loss of porosity.

Beyond the laboratory scale further challenges arise in developing purification and activation processes capable of producing MOFs, consistently with high porosity and at the correct cost base and with minimal environmental impact. The techniques presented in the following sections such as calcination, solvent exchange, supercritical CO₂, freeze drying, microwave heating, ultrasound, UV/Vis (radical and photothermal processes), induction heating, and acid treatment will be compared in this context. A simplified schematic of representative examples of these techniques is shown in Figure 2; corresponding sections for each technique in this review are given in brackets.

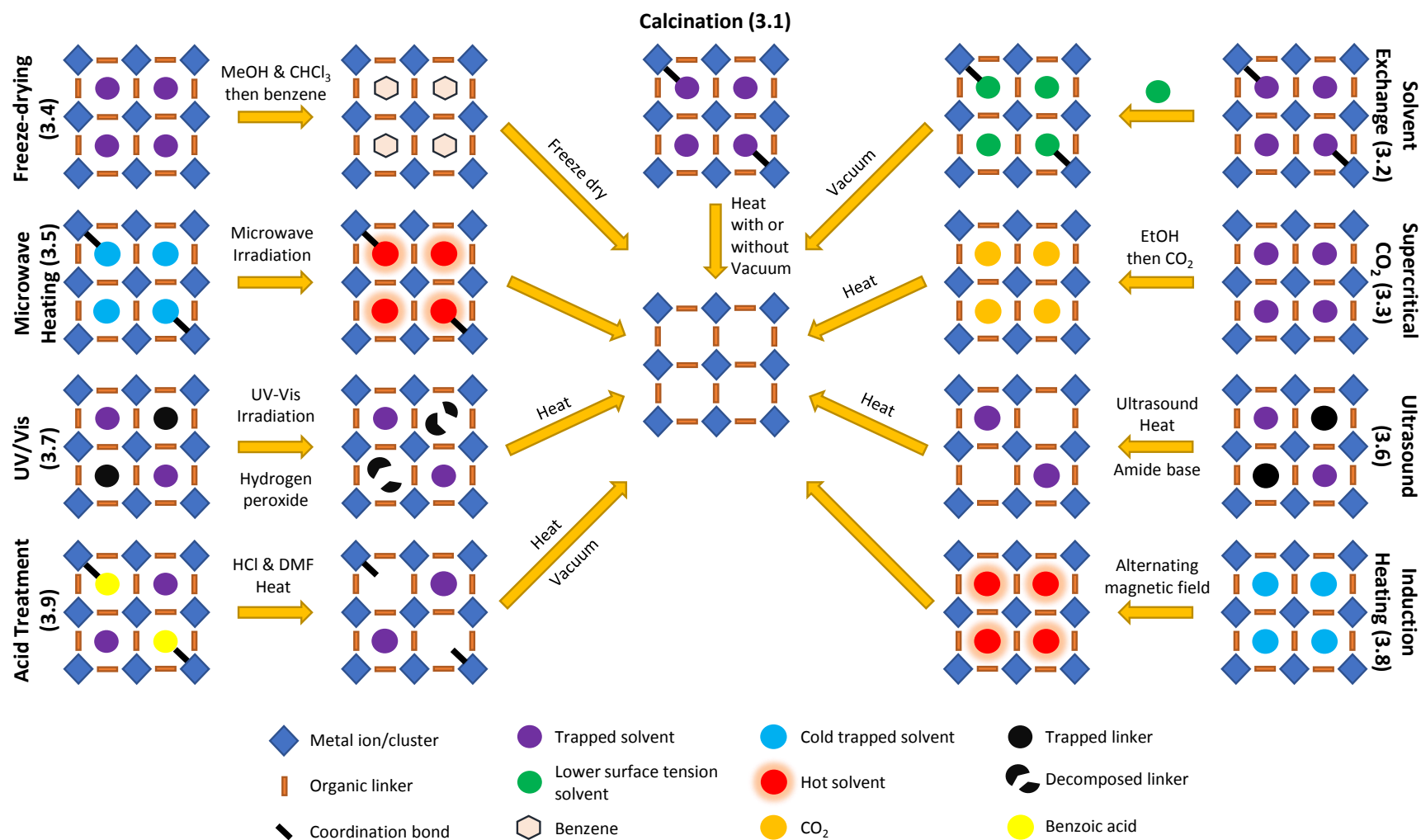


Figure 2: Simplified overview of representative purification and activation techniques including their corresponding sections in this review in brackets

3.1 Calcination

The traditional strategy for activating porous materials such as zeolites and carbons is simple heating under vacuum.¹⁷ This method has been referred to as both calcination, defined by IUPAC as “heating to high temperatures in air or oxygen”,⁵⁵ and conventional heating. Henceforth, we denote this method as “calcination” to indicate heating in both the presence or absence of vacuum; cases where a vacuum is applied will be stipulated. Calcination has also been applied to MOFs and their composites, and studies have been conducted to ascertain the effect of calcination temperature on surface area and pore structure.⁵⁶ Some MOFs successfully activate under this method due to their high stability, such as UiO-66 (composed of $[\text{Zr}_6\text{O}_4(\text{OH})_4]$ clusters with BDC struts $(\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_6)$, activated at 300 °C),⁵⁷ $\text{Zn}(\text{BDC})$ (activated at 140 °C and 5×10^{-5} Torr),⁵⁸ and $\text{Ni}_2(4,4'\text{-bipy})_3(\text{NO}_3)_4$ (activated at 100 °C).⁵⁹ In other cases solvent removal has been shown to cause an advantageous change in crystal structure, *e.g.* $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]\text{H}_2(\text{TC-TTF}) \cdot 2\text{H}_2\text{O}$.⁶⁰ For this MOF, significant structural rearrangements occur on activation (desolvation steps at 50, 80 and 120 °C), leaving an empty-channel framework showing selectivity to guest sorption.

Calcination has also been used to purify and activate MOFs by removing trapped organic linker molecules from within the pores of the MOF. For example, disordered H_2BDC molecules were removed from the 1D rhombic-shaped tunnels of $\text{Al}(\text{OH})(\text{BDC})$ (MIL-53(Al)) by calcination at 330 °C in air for three days.⁶¹ It was later shown that higher BET surface areas could be achieved using a higher calcination temperature of 400 °C (1140 and 1203 m^2g^{-1} for calcination at 330 and 400 °C, respectively).⁶² These temperatures do not result in framework collapse for MIL-53(Al) due to its high thermal stability; thermal decomposition does not begin until 500 °C.⁶¹ Also noteworthy is that H_2BDC sublimes at 402 °C,⁶³ meaning it could potentially be collected during purification/activation and reused without having decomposed. Despite these successes, loss of crystallinity and porosity can occur in MOFs during calcination as a result of high surface tension induced capillary forces created from liquid solvent removal during activation.⁶⁴ This occurs in many MOFs, resulting in calcination being unsuitable for activation.¹⁷ An example of loss of crystal

structure upon activation can be seen in copper porphyrin frameworks.⁶⁵ Calcination may also be unsuitable for MOFs where the temperatures required for linker removal are above the thermal stability of the MOF. For example, we have seen that H₂BDC molecules are effectively removed at 400 °C for MIL-53(Al);⁶² however, MIL-53(Cr) and MIL-53(V), both also containing H₂BDC, are only stable up to 350 °C.⁶¹

Calcination is inherently scalable; however, large amounts of energy and space/footprint are required to heat up sizable volumes of material and careful design considerations are required to ensure even heat distribution otherwise MOF destruction may occur.⁶⁶ Lowering the pressure by applying vacuum can also be difficult as scale increases. Temperatures required can be high (typically >100 °C) and are dependent on the boiling or decomposition temperature of the solvent, the sublimation or decomposition temperature of any trapped linker, and whether solvent molecules or other chemicals are coordinated to metal sites. The process also often takes many hours. For example, without the use of a vacuum, Cu-BTC-MOF (denoted Cu-MOF by Mueller *et al.*⁶⁷) required drying at 120 °C overnight followed by activation at 250 °C,⁶⁷ Zn(BDC) (MOF-2) involves activation at 200 °C for 8 hours⁶⁷, and Cu₃(BTC)₂ (HKUST-1) also requires heating at 200 °C.⁶⁸ Even recently reported MOFs such as [Al₂(OH)₂(C₁₆O₈H₆)](H₂O)₆ (NOTT-300/MFM-300), promising in NO₂, SO₂ and CO₂ capture, still require drying at 50 °C for 18 hours and activating at 120 °C for 15 hours under vacuum (10⁻⁵ bar).^{69,70} The high energy requirements and long timescales make calcination an undesirable technique for use in large-scale MOF production. The process is unfavourable from a sustainability standpoint due to the high energy usage from inefficient conductive heating (indirect). The main benefits of calcination are that it is simple and cost-effective at lab-scale and no additional solvents are required during activation. Furthermore, calcination is a generic method that is applicable widely and is well established.

3.2 Solvent Exchange

One route to avoiding the structural collapse of a MOF during activation is to decrease the capillary forces exerted by the solvent on the framework. This can be done by exchanging the high boiling point solvent used in synthesis, now trapped in

the pores, for one with a lower boiling point. These solvents have weaker intermolecular interactions and lower surface tensions, and hence lower capillary forces.¹⁷ This method would also potentially decrease the energy required during activation, as only mild heating (usually ≤ 60 °C) under vacuum is necessary. This method usually involves first washing the MOF with the reaction solvent to remove uncoordinated linkers or other impurities, then washing and soaking the MOF in a new solvent.⁵³ A soxhlet extraction set up whereby the insoluble porous material is continually washed with hot solvent (typically used for microporous polymers)^{71–74} can also be used for solvent exchange in MOFs, as in $\text{Co}_2(\text{dhtp})$ and $\text{Zn}(\text{mIm})_2$ (ZIF-8).⁷⁵ However, with this technique the energy costs of using or refluxing hot solvents would need to be considered, and could prove higher than that of calcination, depending on the latent heats of evaporation and quantities of solvents used.

The first example of solvent exchange for MOF activation was reported for $\text{Zn}_4\text{O}(\text{BDC})_3$ (MOF-5), where DMF and chlorobenzene from the synthesis step were fully replaced with chloroform. Chloroform can then be removed from the pores within three hours at room temperature and 5×10^{-5} torr without structural damage.⁷⁶ MOF-5 has also been activated by exchanging diethylformamide for acetone followed by heating at 60 °C for 3 hours at <0.2 mbar.⁶⁷ Another example is reported for $\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8\text{TBAPy}_2$ (NU-1000). In this case adsorption and desorption isotherms for N_2 showed that framework collapse had occurred when activated from water, resulting in a much lower adsorption when compared to activation from acetone.⁵³ Further examples of MOFs benefiting from solvent exchange include the IRMOFs,⁷⁷ such as $\text{Zn}_4\text{O}(\text{H}_2\text{N-BDC})_3$ (IRMOF-3) and $\text{Zn}_4\text{O}(\text{TPDC})_3$ (IRMOF-16), which both show greatly improved N_2 uptake when activated from chloroform following solvent exchange from DMF.⁷⁸

A recent study investigated the use of ultra-low (*i.e.* ≤ 20 mNm⁻¹) surface tension solvents to avoid structural collapse in more fragile MOFs.¹⁸ In this example $\text{Zn}_4\text{O}(\text{naphthalene-2,6-dicarboxylate})_{1.5}(\text{biphenyl-4,4'-dicarboxylate})_{1.5}$ (UMCM-9) had previously failed to activate with solvent exchange, undergoing a partial collapse from chloroform (surface tension: 27.2 mNm⁻¹) resulting in a reduced surface area of 1330 m²g⁻¹ compared to the theoretical value of 4900 m²g⁻¹ (calculated from its

structure).⁷⁹ When solvent exchanged with *n*-hexane (surface tension: 17.9 mNm⁻¹), a higher surface area of 4980 m²g⁻¹ was obtained, close to the predicted theoretical value.¹⁸ Similar results were observed for MOF Zn₆(btb)₄(4,4'-bipy)₃(DMF)₅₅(H₂O)₃₂ (FJI-1), where an even lower surface tension solvent, perfluoropentane (surface tension: 9.42 mNm⁻¹), was required for the exchange. In this case activation from *n*-hexane resulted in an undesirable surface area of < 100 m²g⁻¹. When perfluoropentane was used, a surface area of 4890 m²g⁻¹ was measured, comparable to the theoretical value of 4741 m²g⁻¹. This study also reported rapid solvent exchange (minutes rather than days) and demonstrated that the rate of evacuation (between 380 and >225000 torr h⁻¹) had no measurable impact on the surface area.

A detailed study of the effects of solvent exchange and activation on MOF structure was conducted by Dodson *et al.* in 2018.⁸⁰ A range of solvents (chloroform, THF, hexane) and MOFs containing Zn₄O metal clusters (MOF-5, UMCM-9, and [Zn₄O(CVB)₃]₁₃(DEF)·2H₂O (SNU-70)) were investigated. By *in situ* 2D-PXRD monitoring it was found that when structural collapse did occur during activation, it was always during solvent evacuation rather than exchange. It was also noted that 2θ-axis broadening of PXRD peaks was not indicative of framework collapse, as surface area was maintained. It was discovered that broadening may instead be caused by changes in the crystallite size of the MOF during solvent removal, with no decrease in bulk surface area. Retention of surface area was found to correlate, however, with preservation of crystallite orientation measured by a broadening along the β-axis.

An alternative solvent exchange method has also emerged utilising DCM to activate open metal sites in a series of MOFs, removing both pore-filling and coordinating solvent molecules.^{81–84} Open metal sites are desirable for many applications including catalysis, sensing and gas adsorption and separation, and so removing coordinated ligands is an important step in the activation of many MOFs.⁸⁵ Kim *et al.* first showed the use of DCM in activating copper-based MOFs HKUST-1 and Cu₂(BDC)₂ (Cu-MOF-2) without the application of heat.⁸¹ Prior to this report DCM has been popularly used in steps prior to thermal activation by calcination. The authors postulated a mechanism for their activation process whereby DCM replaces the

coordinating solvent on copper, followed by spontaneous de-coordination owing to a low activation energy (room temperature thermal energy) leaving open metal sites. DCM exchange was shown to be effective for the de-coordination of water, ethanol, methanol, acetonitrile and DMF, without needing to apply heat or a vacuum. Kim *et al.* also showed that their DCM exchange process, followed by activation for two hours under vacuum at 25 °C, yields activated HKUST-1 with a surface area comparable to calcination under vacuum (150 °C for 12 h at 10^{-3} torr); *i.e.* $1690\text{ m}^2\text{g}^{-1}$ compared to $1740\text{ m}^2\text{g}^{-1}$, respectively.

The DCM method was further developed by Bae *et al.* for the efficient removal of strongly coordinating solvents, such as DMF, DEF and DMSO; in these cases multiple coordination exchanges were required.⁸² In this instance, the coordinating solvent is first exchanged with acetonitrile, methanol or ethanol, then subsequently with DCM. The process effectiveness was demonstrated with the successful activation of a thermally unstable MOF, $\text{Ni}_2(\text{DOT})$ (Ni-MOF-74). An analogous treatment to DCM has also been conducted with chloroform, which proved effective at activating thermally deformable MOFs in mixed matrices with polymers.⁸⁴ The quick and complete removal of both pore-filling and coordinating solvents at room temperature makes DCM exchange an attractive and promising technique for MOF activation. From a temperature standpoint, this method is desirable for industrial application. However, the need for vacuum is disadvantageous since large and expensive equipment will be required. Further challenges include that it has yet to be tested on a wide range of MOFs and that the process currently requires a moisture-free environment.⁸²

Solvent exchange techniques have shown wide applicability to a range of MOFs. Use of ultra-low surface tension solvents and detailed structural studies pave the way for increasing understanding and possible applications of this method. Furthermore, the milder heating and pressure conditions when compared to calcination are beneficial from an environmental perspective due to reduced energy requirements. However, when considering the scalability and sustainability of the solvent exchange method, thought needs to be given to the types and quantities of solvents involved. The use of many litres of toxic or highly flammable solvents is very unfavourable from an industrial standpoint, incurring high costs and large amounts of waste produced.

Research has been conducted on a range of common solvents to assess their environmental impact and provide a useful selection guide.⁸⁶ Guidelines such as these should be consulted when considering MOF production and processing. If solvents could be minimised and recycled in the process, solvent exchange could become a more viable method for industrial-scale MOF activation. However, this would require introducing processes for separation and collection of solvents, possibly increasing energy costs. Further challenges lie in processing the waste streams containing varying concentrations of different chemicals produced during the washing phases.

3.3 Supercritical CO₂ (SCD)

Alongside efforts to avoid the structural collapse of delicate MOFs by solvent exchange, an alternative approach involving carbon dioxide was developed by Nelson *et al.* in 2008.⁷⁸ Typically, this process first involves solvent exchange with ethanol, then with liquid CO₂. The CO₂-loaded MOF is then heated above the critical point of carbon dioxide (31 °C and 73 atm), held for 30 minutes, then vented over 18 hours. This method was found to result in higher surface areas for a variety of MOFs when compared with calcination or solvent exchange (chloroform or THF) routes.⁷⁸ An example of an SCD experimental set-up and apparatus schematic can be found in Xiang *et al.*⁸⁷ The effectiveness was ascribed to the inhibition of mesopore collapse by removing surface tension and preventing detrimental MOF particle agglomeration, which would block access to micropores by causing their misalignment at particle-particle boundaries.

Since its discovery, SCD has been used to activate a variety of different MOFs. One such example is Cu₃(C₆₀H₂₄O₁₂)(H₂O)₃ (also known as NU-100), which features a hexacarboxylated linker. For this MOF, SCD was found to be the only activation method capable of removing pore blocking solvent molecules without damaging the structure of the MOF.⁸⁸ Yaghi *et al.* further showed the usefulness of this method for activating a range of MOFs with surface areas as high as 6240 m²g⁻¹.⁸⁹ Furthermore, SCD has been shown to activate MOFs with a high capacity for hydrogen storage.⁸⁷ Since MOFs with increasing pore sizes tend to be more prone to framework collapse upon

solvent evacuation, SCD was used to activate NU-109E and NU-110E. These MOFs exhibit surface areas amongst the highest reported to date, 7010 and 7140 m²g⁻¹ for NU-109E and NU-110E, respectively.⁹⁰

Alternative processing arrangements have also been investigated for SCD, such as flow activation, which allows a reduction in sample CO₂ purge time from approximately 16 hours to 30 minutes.^{78,79} A more detailed comparison of the SCD treatment variations to date and the possible impacts of SCD on MOF structures has been reported by Dapaah *et al.*¹⁹ Notably the authors mention that high surface areas may still be achieved without the solvent exchange step prior to liquid CO₂ exchange.

Although SCD has proven useful for activating many MOFs, there are still some materials where the surface areas are lower compared to alternative activation techniques. For example, Cr₃OF(H₂O)₂(BDC)₃ (MIL-101(Cr)) shows a similar BET surface area after purification in 1 M NH₄F solution at 70 °C for 24 hours followed by activation at 100 °C under vacuum overnight when compared to SCD (3350 m²g⁻¹ and 3400 m²g⁻¹ respectively).⁹¹ These results are ascribed to the zeolite-type topology of these MOFs,⁵² *i.e.* they contain both super-tetrahedral cages which may prevent the collapse of the pores by capillary pressure, and also mesopores accessible through microporous windows.^{52,92} However, the BET surface area of MIL-101(Cr) has been reported as high as 4100 m²g⁻¹ after the use of a solvothermal treatment to evacuate free acid from within the pores.⁹³ In addition to MOFs containing trapped acid, those with open/coordinatively unsaturated metal sites may require heating in addition to SCD processing to remove coordinated solvents, as they can become strongly attached to metal centres.⁹⁴

SCD is reportedly a scalable technology, which is cost-competitive and non-toxic.¹⁷ However, SCD does require multiple steps including varying the temperature and pressure at different stages, which could render it an energy intensive and lengthy process. The comparative energy requirements of the heaters, chillers, and pumps per kilogram of CO₂ have been assessed by Martin *et al.* when using SCD for the extraction of oil seed rape.⁹⁵ The aforementioned flow SCD method may be quicker and more appropriate at an industrial scale but this route requires a specialised and

expensive set up.⁵³ Often additional solvents are required prior to activation with CO₂, which may also have a potentially negative impact on the sustainability of the technique. CO₂ is generally considered a 'green' solvent, and its use in industry can result in cleaner and less expensive processes.⁹⁶ Further sustainability improvements may be possible if CO₂ could be sourced from the environment (e.g. carbon capture) and reused along with any other solvents involved in SCD activation.

3.4 Freeze-drying

Freeze-drying is a technique well-known in the porous materials industry. This method involves removal of frozen solvents from a porous host *via* sublimation under vacuum, resulting in a solvent-free porous material.⁹⁷ This process was first investigated for MOFs by Ma *et al.* in 2009.⁹⁸ They showed that replacement of high boiling-point solvents (DMF and DEF) in the pores and channels of two new 4,4-connected MOFs with benzene, followed by freeze-drying, could be used to successfully activate these MOFs. This method involves first washing the MOFs with methanol and chloroform, followed by several benzene washes and soaking in benzene overnight. The samples were then frozen at 0 °C and underwent three freeze-thaw cycles before drying in a vacuum for 24 hours in an ice bath, 24 hours at room temperature and 16 hours at 60 °C. The result was that MOFs containing elongated ligands with large channels (19.5 × 7.0 Å along the crystallographic *a* axis) could be activated without framework collapse. Ma *et al.* reported that the sublimation step bypassed the liquid-to-gas transition, avoiding the surface tension induced capillary forces which can lead to damage. The MOFs tested (denoted by Ma *et al.* as compound 1 and 2) showed greatly increased BET surface areas from freeze-drying (1560 and 1020 m²g⁻¹ for compound 1 and 2, respectively) compared to solvent exchange then vacuum-drying at 60 °C overnight (526 and 791 m²g⁻¹ for compound 1 and 2, respectively). Hydrogen uptake capacities were also higher for the freeze-dried materials (1.42 and 1.73 wt % compared to 0.78 and 1.26 wt % vacuum-dried for compounds 1 and 2, respectively). Also noteworthy in this study was the change in the PXRD pattern of the freeze-dried MOFs compared to that of the pristine samples. This was ascribed to a phase change caused by a breathing effect, which has also been observed in other materials.⁹⁹

Later work by He *et al.* showed that cyclohexane could be used instead of benzene as the freeze-drying solvent; in this case for the activation of a novel MOF containing a nanosized ligand, $[\text{Zn}_2\text{L}(\text{imidazole})] \cdot 7(\text{DMF})$ where $\text{L} = \text{Tris}((4\text{-carboxyl})\text{phenylduryl})\text{amine}$ (FIR-3).¹⁰⁰ The porosity of this MOF was found to be dependent on the activation route with surface areas of 24.3, 266.0, and 497.2 m^2g^{-1} reported for calcination, freeze-drying, and SCD, respectively. Although SCD processing resulted in the highest surface area, freeze-drying still showed a large improvement in surface area compared to calcination; furthermore, cyclohexane is much less toxic than benzene, thus this work represents a significant improvement in the freeze-drying technique.

The final example discussed herein of MOF activation by freeze-drying involves the production of a nano-version of HKUST-1 (particle size 100 nm to 5 μm).²⁰ In their work, Wee *et al.* utilised freeze-drying to not only remove ethanol solvent molecules but also limit MOF crystal growth.²⁰ This enabled the production of HKUST-1 with high crystallinity and porosity and a narrow particle size distribution. Wee *et al.* also showed that the freeze-dried nano-version of HKUST-1 outperformed hydrothermally synthesized HKUST-1 in catalysing the ring opening of styrene oxide with methanol (90% compared to 2% conversion), hypothesised by the authors to be a result of the shorter diffusional pathways.²⁰

Currently only limited reports of MOF activation by freeze-drying exist in the literature, therefore, it is not yet clear how general this method will be for other MOFs. Furthermore, although the general principles of solvent exchange and freeze-drying are well established, further research is required to understand the effect of freeze-drying on possible crystal phase changes *e.g.* breathing effects.⁹⁹ Beyond the laboratory, freeze-drying is commonly used in both the food¹⁰¹ and biopharmaceutical¹⁰² industries, though it can be very demanding from an electricity standpoint.^{102,103} Further considerations for industrial scale freeze-drying processes include: potential heat and mass transfer challenges;¹⁰⁴ the amount of heating and refrigeration required; and the length of the process, which can result in high electricity costs and associated environmental burden. This burden could be reduced if the electricity used came from a renewable source. Capturing the exchanging and

subliming solvents and reusing them would also serve to increase the sustainability of the process but may prove difficult due to the mixtures of solvents produced. It is, therefore, beneficial to limit the number of different solvents required, to simplify the collection and reuse process.

3.5 Microwave Heating

Microwave technology has been used extensively in the synthesis of porous materials^{34,105,106} and for regeneration of adsorbents (*e.g.* silica,¹⁰⁷ zeolites,¹⁰⁸ activated carbon¹⁰⁹) after use, where it has demonstrated great advantages over conventional heating methods owing to improved energy and time efficiency as a result of targeted heating. However, only recently microwave heating has been considered and investigated as a purification and/or activation technique for porous materials post-synthesis (rather than during synthesis or for regeneration). For example, Campbell *et al.* used a microwave reactor to purify as-synthesised COF-5 ($C_9H_4BO_2$, where COF is an acronym of covalent organic framework) by heating the material in dried acetone (55 °C, 20 min, 200 W) to extract any starting materials or impurities trapped in the porous structure.¹¹⁰

COFs are porous crystalline materials constructed from light elements (hydrogen, nitrogen, boron, carbon and oxygen) that are held together by strong covalent bonds.¹¹¹ The purification procedure reported by Campbell *et al.* is capable of removing the pore-blocking constituents without causing framework collapse. The BET surface area was measured after activation at 90 °C and 10^{-5} bar, and a substantial increase in the surface area of the material was observed when the purification step was repeated, from $901\text{ m}^2\text{g}^{-1}$ (as synthesised) to $1467\text{ m}^2\text{g}^{-1}$ (after first extraction) and $2019\text{ m}^2\text{g}^{-1}$ (after second extraction). A similar procedure was successfully used for $C_{25}H_{16}B_4O_4$ (COF-102), involving microwave heating in THF.¹¹⁰ Microwave synthesis and purification was further investigated for COF-5 by Ritchie *et al.* in 2010.¹¹² In this case microwave synthesised COF-5, which was subsequently purified by microwave irradiation in acetone, exhibited a higher surface area compared to purification by conventional acetone washing and filtering or simple desiccator drying. After activation at 120 °C and 10^{-5} bar, the measured surface areas

were 2335, 1927, and 1404 m²g⁻¹ for microwave, acetone washing, and desiccator drying purification methods, respectively.

The first application of microwave-assisted purification and activation in MOFs was reported in 2017, with activation and modulator removal in zirconium MOFs.¹¹³ Three MOFs; namely Zr₆O₄(OH)₄(BTC)₂(COOH)₆, MOF-808; Zr₆O₈(NDC)₃(CH₃COO)₂(C₂H₅OH)₇(DMF), DUT-84; and UiO-66; were successfully activated (an acetic acid modulator and organic solvent was removed from the frameworks) by microwave irradiation in water (150 °C, 20 min), followed by washing and vacuum filtration. All MOFs showed partial removal of the acetic acid modulator, and complete extraction of DMF used in synthesis by proton NMR. However, TGA data show that the activated frameworks contained some adsorbed moisture or other residual solvents. MOF structural integrity was retained during activation, and the catalytic activity of the MOFs for the hydrolysis of a chemical warfare agent simulant was shown to increase compared to the non-activated counterparts.

Further progress in microwave activation was achieved in 2019 by Lee *et al.*, for a range of MOFs.²¹ In their work proton NMR showed that complete activation (removal of both coordinating and pore-filling solvent) was achieved for HKUST-1 from a range of solvents (methanol or ethanol, acetonitrile, and DMF in 4, 8, and 35 minutes, respectively) under microwave irradiation of powder samples (600 W). Methanol proved to be the most efficient solvent for microwave activation in this study, ascribed by the authors as a combination of its low coordination strength and boiling point, and high dissipation factor compared to the other solvents tested. The authors also showed that solvent exchange with methanol prior to microwave activation led to a considerable reduction in microwave activation times for a range of MOFs compared to their DMF-containing analogues, specifically: 35 to 4 min for HKUST-1; 10 to 3 min for UiO-66; and 5 min for Ni, Mg, Co and Cu variants of MOF-74. We also add that a further benefit of solvent exchange from DMF is the avoidance of decomposition of DMF into carbon monoxide and dimethylamine. Furthermore, Lee *et al.* also highlighted a 100-fold reduction in energy requirements for activation of HKUST-1 *via* their method compared to thermal activation; *i.e.* energies of 5400

and 5800 W h for thermal activation from methanol and DMF, respectively *c.f.* 51 and 385 W h for microwave activation from methanol and DMF, respectively.²¹

As with freeze-drying, very limited examples of microwave purification and activation of MOFs exist, therefore, further research into the generality of the approach is required. It is likely that some MOFs and/or solvents may not be suited to microwave heating (*e.g.* toluene, which can be considered as microwave transparent)¹¹⁴, and the effect of microwave heating on delicate frameworks remains unknown.

Microwave technology offers energy-efficient rapid and selective heating with the potential for energy and cost savings on an industrial scale,³⁴ as seen in mineral processing.^{115,116} It also lends itself well to continuous processing. These factors all make the method more sustainable compared to other techniques such as calcination. However, scaling up microwave systems does require an understanding of the fundamental parameters to be applied in the design stage, such as dielectric properties, microwave penetration depth, and power density in the heated phase.³⁴ If these parameters are not well understood there can be difficulties in controlling the temperature, non-uniform heating, and limited microwave penetration depth.¹¹⁷ Microwave heating has previously been used on an industrial scale for adsorbent regeneration for various materials including polymeric adsorbents, activated carbon and alumina.¹¹⁸ Patents are also available in this area, for example, the microwave regeneration of saturated solid noncarbon adsorbents.¹¹⁹

3.6 Ultrasound (US)

Metal carboxylate MOFs have been widely studied due to their high porosities and stability in water and ambient conditions.¹²⁰ Among the most popular are the MIL-53⁶¹ series and HKUST-1.¹²¹ They contain 1,4-benzenedicarboxylate or 1,3,5-benzenetricarboxylate ligands respectively. An issue with many MOFs containing carboxylate ligands is that the corresponding acids can become trapped in the channels of the MOFs, as previously mentioned for MIL-53(Al) in section 3.1.

Few examples of MOF purification by ultrasound (US) are reported; in these cases, US has primarily been used for purification of MOFs constructed from carboxylate

linkers resulting in solvated frameworks. Furthermore, the activation of MOFs is yet to be achieved using US. In 2009, Haque *et al.* investigated use of US treatment for the low temperature (< 100 °C) removal of unreacted H₂BDC linkers from selected MOFs in the MIL-series.¹²⁰ The authors showed that MIL-53(Al) containing unreacted H₂BDC linker can be purified at 70 °C by the addition of amide bases such as DMF and DMA and US treatment for one hour. Activation was confirmed after drying (150 °C, 15 h, without vacuum) by nitrogen adsorption and XRD. The versatility of their method was demonstrated by purification of further MOFs, namely MIL-53(Cr), VO(BDC) (MIL-47(V)), and MIL-101(Cr). Haque *et al.* also commented that their method may be applicable to MOFs where the temperatures required to remove unreacted linkers *via* calcination could lead to structural damage of the framework. Later in 2016, Israr *et al.* showed that HKUST-1 could also be purified with US treatment whereby unreacted chemicals were removed in 30 minutes at low power (150 W).¹²² This accelerated removal of unreacted chemicals was attributed to the rapid dissociation and diffusion under US.

A similar strategy was developed by Rubio-Martinez *et al.* using megasonics, a high frequency (2 MHz) form of ultrasound, for the purification of MIL-53(Al) and its analogue Al(OH)(fum)·3.5H₂O (also known as Al-fumarate) in continuous flow.²³ Both MOFs were purified by sequential washing in water and ethanol under US at 10 minutes per wash and for a total of 5 washes. US also facilitated separation of MOFs from the solvents. More details of their experimental set-up and a schematic of the apparatus can be found in their paper.²³ In the case of MIL-53(Al), purification using US followed by activation (under dynamic vacuum at 10⁻⁶ torr and 140 °C for 8 hours) resulted in a material exhibiting a surface area of 1183 m²g⁻¹, which the authors note is a 47% increase compared to purification by standard centrifuge washing. The authors attributed the increase in surface area to improved removal of excess organic ligands from the MOF pores as a result of enhanced mass transfer from acoustic streaming during megasonic application. In addition to their megasonic downstream separation and purification method, Rubio-Martinez *et al.* followed a water-based continuous flow synthesis to first prepare the two MOFs. This combination of flow

synthesis and megasonic purification is an ideal candidate for industrial scale MOF production owing to benefits such as fast reaction time and cost-effectiveness.

From these limited examples, it can be deduced that US purification offers a potentially sustainable process, primarily due to low energy and solvent quantity requirements. However a major challenge with this route lies in achieving a uniform ultrasound distribution when scaling up beyond the laboratory; further information concerning this can be found in a recent review by Dong *et al.*¹²³ A further drawback of US purification is that it has so far been applied to very few MOFs. These limited studies, except for one example regarding ZIF-8,¹²⁴ involve MOFs comprised of carboxylate-linkers. Further research is also required to determine whether US or megasonics can be used for purification of fragile MOFs. The low bulk temperatures typical of this technique (<100 °C) may prove particularly useful in the purification of thermally unstable MOFs, though further activation is required to produce an empty framework.

3.7 UV-Vis

Another low-energy, environmentally friendly purification and activation method recently applied to certain MOFs is UV-Vis irradiation. In 2014, Nguyen *et al.* reported the treatment of MIL-53(Fe) with aqueous hydrogen peroxide under UV-Vis irradiation, which resulted in the decomposition of unreacted H₂BDC, thus enabling its extraction from the MOF.¹²⁵ This purification procedure was carried out in open air room temperature conditions, using an Osram Eversun (L 40 W/79 K) UVA source 20 cm from the MOF mixture. The H₂BDC decomposition process was monitored as a function of hydrogen peroxide concentration by frequent sampling for FT-IR analysis. The maximum investigated concentration of 75 mM aqueous hydrogen peroxide solution was found to be most effective, with complete decomposition of H₂BDC observed within 60 minutes. After filtration, thermogravimetric analysis showed that both DMF (the synthesis solvent) and H₂BDC had been removed from the UV-Vis treated MIL-53(Fe) material leaving only water. In addition, PXRD showed the MOF to be undamaged. The suggested mechanism for UV-Vis purification from Nguyen *et al.*¹²⁵ is based on the photocatalytic activity of MIL-53(Fe) and production

of hydroxyl radicals described by Ai *et al.* for the degradation of organic dyes in MIL-53(Fe) with hydrogen peroxide.¹²⁶

In 2018 Espin *et al.* reported a photothermal activation process for MOFs.²² This method relies on light-to-heat conversion, where UV-Vis irradiation causes heat to be generated locally within the material which evaporates solvent molecules. This principle is well known, and has already been applied, for instance, in water evaporation from light-absorbing nanoparticles.¹²⁷ Photochemistry has also previously been utilised in MOF applications, such as the use of concentrated sunlight in regenerating adsorbed carbon dioxide from MOFs containing light-responsive organic linkers,¹²⁸ or silver nanocrystals.¹²⁹ Espin *et al.* showed that several MOFs containing absorption bands in the range 300 to 650 nm can be heated to *ca.* 120-170 °C in < 5 minutes by UV-Vis irradiation of powder samples under a stream of argon gas, resulting in removal of both trapped and coordinated solvent molecules.²² Experimental details and a photograph of the equipment set-up can be found in the supporting information of their paper.²² The effectiveness and efficiency of the localised heat generation by UV-Vis irradiation for HKUST-1 activation was demonstrated by the superior surface area achieved in comparison to the material calcined at the same temperature. The authors also commented that successful photothermal activation of IRMOF-3, which typically requires SCD activation in order to achieve an optimum surface area of 2850 m²g⁻¹, may indicate the applicability of their activation method for fragile MOFs.

An obvious limit of approaches making use of UV-Vis purification and/or activation is that MOFs must exhibit a photochemical response for the technique to be effective. Espin *et al.* demonstrated that MOFs which do not exhibit an absorption band in the 300 to 650 nm range, such as UiO-66 and ZIF-8, only show a mild photothermal effect upon irradiation resulting in incomplete activation and low BET surface areas compared to previous reports (UiO-66: 424 m²g⁻¹ *c.f.* 1580 m²g⁻¹; ZIF-8: 1130 m²g⁻¹ *c.f.* 1400-1500 m²g⁻¹).²² Another factor to be considered is the penetration depth of radiation through the material required to achieve homogeneous purification or activation, and the attenuation of photon intensity with path length.¹³⁰ In the case of photothermal activation, it may be difficult to control the resultant temperature, and

since this method involves heating, its applicability to other thermally unstable MOFs requires further investigation. Although the hydroxide radical purification approach taken by Nguyen *et al.* does not involve any heating, a final activation step would still be required to produce an empty framework. In addition, only one MOF has shown to be effective in this technique so far, and the radical process may not work with many other MOFs, particularly those sensitive to hydroxyl radicals.¹²⁵ Since the H₂BDC linkers decompose in this process, there is also limited scope for their reuse.

Both UV-Vis procedures could be considered sustainable due to their time and energy efficiencies, and both can be processed at room temperature and pressure without the use of toxic solvents. In comparison to many of the previously discussed purification and activation methods herein, these two procedures require less solvents, less expensive equipment, less energy and less time, making them promising techniques for use on an industrial scale. In addition, UV-Vis irradiation technology is easily scaled up and could be incorporated into continuous flow processes for the large-scale production of MOFs.

3.8 Induction Heating

Having already considered the efficient localised heating offered by both microwave and UV-Vis technologies (sections 3.5 and 3.7, respectively), it is also worth mentioning the possibility of using magnetic induction heating for MOF purification and activation. Although the use of induction heating as a purification or activation process is yet to be reported for MOFs, it has been used in a similar principle to release adsorbed gases from inside these materials. The use of an alternating magnetic field for controlled desorption was first shown with zeolites, silica, and activated carbon.¹³¹ Later, Magnetic Induction Swing Adsorption (MISA) was applied to magnetic framework composites (MFCs) comprised of MOFs and ferri-magnetic nanoparticles for the release of captured carbon dioxide.¹³² MISA proved incredibly time and energy efficient, and promising for industrial scale use.^{133,134} MISA has also been combined with a UV light irradiation method resulting in record levels of 96.8% of adsorbed carbon dioxide being released on demand.^{128,135} The MISA process has

also found successful application in methane separation and adsorption from landfill gas,¹³⁶ and oxygen capture and delivery.¹³⁷

With the effective use of magnetic induction heating in both the production³⁵ and regeneration of MFCs,¹³⁸ it is plausible that the same method could be employed for the purification and activation of thermally stable MOFs. From a sustainability perspective this localised heating method is much more time and energy efficient compared to calcination and thus requires less energy and operational costs. However, a key drawback of induction heating is the requirement of the material to interact with a magnetic field, which would limit its application to specific MOFs and MFCs. However, given the major advantages that magnetism can bring for the industrial application of MOFs,¹³⁹ it is possible that more magnetic MOFs and MFCs will be produced in the future. If so, the use of induction heating for purification and activation may then become a more practical option.

3.9 Acid Treatment

The final technique assessed in this review is acid treatment, which is frequently followed by calcination under vacuum to give the activated MOF. Acid treatment has often been used for zirconium based MOFs.^{140–142} These MOFs typically require the use of modulators during synthesis for crystal and particle size control, which can then become trapped within the framework.¹⁴³ For example, Mondloch *et al.* showed that it was necessary to expose NU-1000, previously mentioned as an example of solvent exchange in section 3.2, to a HCl/DMF mixture at 100 °C for 24 hours in order to remove benzoic acid coordinated to the Zr₆ nodes, leaving behind terminal -OH groups.¹⁴⁰ This mechanism likely involved the protonation of coordinated benzoate ions which could not be driven off by heat, allowing benzoic acid to be removed as the neutral species.¹⁷ The HCl impurities were then removed by DMF and acetone washes, with final activation at 120 °C under vacuum for 12 hours.¹⁴⁰ The acid treatment used for NU-1000 is adapted from a procedure reported by Feng *et al.* who found that the porosity of a zirconium metalloporphyrin MOF, Zr₆(μ₃-O)₈(OH)₈(TCPP)₂ (PCN-222), could be increased by applying a dilute acid solution as a treatment prior to thermal activation.¹⁴¹

Acid treatment may prove useful for removing many different conjugate bases (in addition to benzoic acid) bound to a range of metal nodes within MOFs, which typically occurs during modulated synthesis of MOFs.¹⁴⁴ However, since thermal activation is still required after acid treatment, the overall technique may not be applicable to thermally sensitive MOFs. In addition, the same sustainability and scalability challenges apply as with calcination (e.g. high energy, space, and time requirements). Treatment with acid also requires the MOF to have high chemical stability to prevent hydrolysis and framework collapse.¹⁴⁵ This stability is often found in Zr-based MOFs due to the high coordination numbers of the metal ions and strong Zr-O coordination bonds between metal ions and donor ligands.^{145,146}

4 Assessment of Purification and Activation Techniques

In this section we provide a comparative summary of the purification and activation techniques discussed in this review, from technical, sustainability, and scalability perspectives, alongside a brief discussion on costs. Examples of MOFs purified or activated by the techniques described herein and a summary of important considerations when choosing a particular technique (*e.g.* demonstration of the technique for removing organic linkers or activating fragile MOFs) are given in Table 1. It is hoped that these comparisons will aid future decision-making concerning MOF purification and/or activation at the laboratory scale and beyond.

Table 1: A comparison of purification and activation techniques and reported information from the literature. Relevant sections in this paper for each technique are given in brackets in column 1.

Technique	Key MOF examples	Solvents removed examples	Reported to remove organic linkers	Reported to remove coordinated solvents/ chemicals	Reported use with 'fragile' MOFs	Reported to fully activate MOFs	Ref.
Calcination (3.1)	UiO-66; MOF-2; Ni ₂ (4,4'-bipy) ₃ (NO ₃) ₄ ; [Co ^{II} (H ₂ O) ₆]H ₂ (TC-TTF)·2H ₂ O	DMF; H ₂ O	✓	✓	✗	✓	57–60,67
Solvent Exchange (3.2)	MOF-5; Co ₂ (dhtp); ZIF-8; NU-1000; IRMOF-3; IRMOF-16; UCMC-9; FJI-1; SNU-70; HKUST-1; Cu-MOF-2; Ni-MOF-74	DMF; DEF; Chlorobenzene; DMSO; MeCN; MeOH; EtOH; H ₂ O	✓	✓	✓	✓	18,53,67, 75–78,81–84
Supercritical CO ₂ (3.3)	IRMOF-3; IRMOF-16; UCMC-9; NU-100; NU-109E; NU-110E	DMF	✗	✗	✓	✓	19,78,87–90
Freeze-drying (3.4)	Cu ₂ (L)(H ₂ O) ₂ ^a ; FIR-3; HKUST-1	DMF; DEF; H ₂ O; EtOH	✗	✗	✓	✓	20,98,100
Microwave Heating (3.5)	MOF-808; DUT-84; UiO-66; HKUST-1; MOF-74	DMF; MeCN; EtOH; MeOH	✗	✓	✗	✓	21,113
Ultrasound (3.6)	MIL-53; MIL-47; MIL-101; HKUST-1	DMF; DMA	✓	✗	✗	✗	23,120,122
UV/Vis – radical (3.7)	MIL-53(Fe)	DMF	✓	✗	✗	✗	125
UV/Vis – photothermal (3.7)	HKUST-1; UiO-66-NH ₂ ; IRMOF-3; Fe-MIL-101-NH ₂ ; ZIF-67; CPO-27	DMF; EtOH; MeOH; H ₂ O	✗	✓	✓	✓	22
Induction Heating (3.8)	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Acid Treatment (3.9)	NU-1000; PCN-222	N/A	✗	✓	✗	✗	140,141

^aL-H₄: methanetetra(*p*-benzoic acid) or methanetetra(biphenyl-*p* carboxylic acid)

Table 1 indicates a starting point for purification and activation method selection based on the desired outcome/requirements of the MOF under consideration. For example, procedures which are reported to remove coordinated solvents, such as microwave heating or UV/Vis irradiation, should be considered for producing MOFs with open metal sites. For thermally unstable MOFs, techniques which require minimal/no heating should be tested, such as solvent exchange or US exposure. For MOFs liable to framework collapse from surface tension capillary forces, techniques which have been tested on fragile MOFs should be examined, such as supercritical CO₂ processing or solvent exchange. If the MOF pores are blocked with organic linker molecules, US or UV/Vis irradiation could be tried.

Another key consideration when comparing techniques is their sustainability and scalability. If the procedure to synthesise, purify, and activate a MOF is considered unsustainable or unscalable, it is unlikely to be adopted at an industrial scale. Table 2 shows a qualitative analysis of purification and activation techniques, considering the benefits and challenges of each alongside an assessment of sustainability and scalability. Due to a lack of published data, a meaningful quantitative assessment of the various techniques has not been possible. As such, a traffic light system has been used to show the current approximate level of development from technical, sustainability, and scalability perspectives for each technique using calcination as a baseline. Both the benefits and challenges of each perspective are considered. Green implies a higher level of development compared with calcination, orange a similar level, and red a lower level. Calcination has been chosen as the baseline for comparison since it is the most established and is used for other porous materials such as carbons and zeolites on an industrial scale (see Section 3.1). When considering which technique to try from those which may be suitable for a MOF based on Table 1, Table 2 could then be used to choose the most appropriate route with respect to sustainability and scalability.

The cost of MOF synthesis, purification and activation is another important factor when exploring industrial scale production. Equipment (capital and operational), material and energy costs need to be considered when comparing procedures. A techno-economic analysis of four MOFs (MOF-5, HKUST-1, Mg-MOF-74 and Ni-MOF-

74) and three production routes (solvothermal, liquid assisted grinding, and aqueous) was conducted by DeSantis *et al.* in 2017.¹⁴⁷ They found that solvents are a major cost contributor (40-80% of material costs, which are 50-90% of the total costs), even when assuming a 90% solvent recycle rate. Although they looked primarily at synthesis, the principles they employed would likely also apply to the purification and activation steps. Techniques which use less solvent or those that allow solvents to be more easily recovered and reused are expected to be much cheaper on an industrial scale. DeSantis *et al.* also drew attention to cost saving opportunities through the reduction of temperature and processing times, highlighting that high equipment capital costs can be less impactful than high energy requirements.¹⁴⁷ This point should also be considered for large-scale purification and activation procedures, where high energy costs may prove more detrimental than expensive equipment set-ups.

Table 2: A comparison of purification and activation techniques, including an assessment of sustainability and scalability. The traffic light system shows an evaluation of the benefits and challenges and current level of development for each technique, in the three categories of technical level, sustainability, and scalability. Calcination has been used as a baseline for comparison, with green implying a higher level of development, orange a similar level, and red a lower level.

Technique	Technical Benefits	Technical Challenges	Sustainability Benefits	Sustainability Challenges	Example of technology scale in other applications	Scalability challenges for MOF purification or activation
Calcination (3.1)	Simple on lab-scale; Typically only involves 1 step	Possible loss of crystallinity and porosity due to capillary forces; some MOFs are sensitive to thermal decomposition	No additional solvents needed; Cheap on lab-scale; Potential to collect and reuse linkers/solvents	High energy, footprint, and time requirements; Potentially high OPEX	45,000 kg/h Model production capacity of an alumina rotary calciner ¹⁴⁸	Difficult to scale use of vacuum
Solvent Exchange (3.2)	Decreased capillary forces, less likely to cause framework collapse; Applicability to a wide range of MOFs and solvents	Still requires some level of heating and/or reduced pressure; Moisture-free argon-charged glove box required for DCM exchange	Reduced energy requirements due to removal of a lower boiling point solvent	Requires additional solvent; Some solvents are expensive or toxic; Difficult to collect solvents for reuse as mixed together	1 kg/h Solvent exchange in a modular continuous-flow production of an active pharmaceutical ingredient intermediate ¹⁴⁹	Difficult to scale use of vacuum; Processing large volumes of solvents which may be mixtures; Moisture-free atmosphere required for DCM exchange
Supercritical CO ₂ (3.3)	Negligible surface tension so applicable to fragile MOFs; Reportedly a scalable technology; Applicability to a wide range of MOFs	MOFs containing open metal sites require additional heating to remove coordinated solvent; Specialised set up required	Non-toxic; CO ₂ could be sourced from the environment through carbon capture; Flow processing possible	Potentially high energy and time costs from multiple stages, high OPEX; Solvent exchange often required prior to CO ₂ activation, difficult to collect solvents for reuse; High CAPEX	40 kg/h CO ₂ flow rate in a pilot plant pump used for extraction of oil seed rape ⁹⁵	Handling large volumes of solvents; Specialist CO ₂ handling equipment required
Freeze-drying (3.4)	Sublimation avoids surface tension induced capillary forces preventing framework collapse	Unknown effects of crystal phase changes caused by the breathing effect; Not yet tested on a range of MOFs	N/A	Very energy and time demanding, high OPEX; Multiple solvents required, difficult to collect for reuse; High CAPEX	2,845 kg/h Input for a cylindrical chamber multi-zone continuous freeze-drying plant, used in the food and beverage industry for products such as instant coffee ¹⁵⁰	Handling large volumes of solvents; Potential heat and mass transfer issues for scale up beyond laboratory

Microwave Heating (3.5)	Quick process	Some MOFs and solvents may not be suited to microwave heating; Possible framework collapse with more fragile MOFs (yet to be determined)	Small plant footprint; Short heating times; Continuous processing possible; Energy-efficient and targeted heating; Solvent exchange not required	Potentially high CAPEX	100,000 kg/h Throughput of copper ore in a 100 kW continuous pilot scale microwave treatment system on a mine site ¹⁵¹	Limited microwave penetration depth; Difficult to control temperature; Dielectric constants are variable giving non-uniform heating
Ultrasound (3.6)	Low temperatures could be of benefit to thermally unstable MOFs	Predominantly applied to carboxylate MOFs; Unknown effects on fragile MOFs; Further activation required	Low energy process; Low solvent requirements; Low OPEX and CAPEX; Works in water-based flow set up	Amide bases required to remove unreacted linkers	50 kg/h Paint flow through an ultrasound reactor to enhance pigment dispersion ¹⁵²	Difficult to get uniform ultrasound distribution upon scale up beyond laboratory
UV/Vis – radical (3.7)	Simple open-air, room temperature set up; Quick process	Only tested with one MOF; Radical process may not be applicable to other MOFs; Further activation required	Low energy and cheap process, low OPEX; Doesn't require additional solvents; Low CAPEX	Waste generated from organic linkers as they decompose; Needs a sustainable UV source	3 kg/h Product from a 2.2 kW continuous-flow large-scale photoreactor containing 440 m of PFA capillary tubing with a 3.5 L volume ¹³⁰	Penetration of UV light and attenuation of photon intensity with path length
UV/Vis – photothermal (3.7)	Simple, quick, single-step process	Only effective for MOFs with a photochemical response; Heating may damage thermally unstable MOFs	Low energy and cheap process, low OPEX; Doesn't require additional solvents; Low CAPEX	Needs a sustainable UV source	3 kg/h Product from a 2.2 kW continuous-flow large-scale photoreactor containing 440 m of PFA capillary tubing with a 3.5 L volume ¹³⁰	Difficult to control temperature; Penetration of UV light and attenuation of photon intensity with path length
Induction Heating (3.8)	Rapid and scalable technique	MOF must interact with magnetic field; Heating may damage thermally unstable MOFs; Yet to be tested for MOF purification or activation	Energy efficient heating; Low OPEX; Potentially low CAPEX	N/A	135 kg/h Treatment rate for iron in a continuous induction melter with a graphite-packed bed ¹⁵³	Non-uniform heating
Acid Treatment (3.9)	Helps to remove coordinating chemicals	MOFs require high chemical stability; Further activation required	N/A	Acid waste produced	N/A	Handling large volumes of acid waste

5 Conclusions and Future Outlook

The last two decades have seen substantial advancement in the field of MOFs, both in the discovery of new MOF structures and the expansion of their functional properties. Crucial to unlocking the potential of MOFs in real-world applications is the ability to produce them at the required scale, cost base, and in a sustainable manner. Today's enviro-economic situation has led to growing recognition and adoption of the circular economy concept in all industries, and as a result the scientific and engineering community are developing increasingly benign MOF production routes. Although MOF synthesis techniques are well reported and scalability and sustainability assessments have been made, the final key steps in producing MOFs, purification and activation (without which MOFs are essentially useless), are often overlooked.

In this review we have evaluated the technical benefits and challenges of current methods of MOF purification and activation including against principles from the circular economy model such as scalability, waste reduction, material reuse, energy efficiency, and environmental impact. Although purification and activation steps such as calcination and solvent exchange (sections 3.1 and 3.2, respectively) are well established, they are demanding from chemical use, time, and energy perspectives. Furthermore, the harsh conditions involved in these methods can lead to collapse of the MOF structure. To overcome these challenges, ultra-low surface tension solvent exchange, supercritical CO₂, and freeze-drying techniques have been developed. Additionally, substantial improvements in time and energy efficiency compared to calcination and solvent exchange routes can be achieved using ultrasound (section 3.6) and technologies based on targeted heating such as microwave and UV-Vis (sections 3.5 and 3.7). However, further research is required to determine the applicability of targeted heating techniques to a wide range of MOFs. Another area for consideration is the opportunity for capturing and reusing the solvent and/or organic linkers left over after purification and/or activation. On an industrial scale, the quantities of solvent and unreacted linker are likely to be significant; waste and cost may be reduced if the processes were able to recover and reuse these

components *e.g.* as feedstocks in the MOF synthesis. Finally, evaluation of purification and activation of MOF by life cycle assessment (LCA) and techno-economic analysis (TEA) would ensure that processes developed are sustainable on a life cycle basis, which is crucial to transitioning MOFs from the lab to industrial production and application.

MOFs are a class of materials that have many potential applications within a wider future circular economy; given the current stage of MOF development and commercialisation, there is also an opportunity for the MOF industry to develop as a circular one.

6 Conflicts of Interest

There are no conflicts of interest to declare.

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Appendix 2

Rapid synthesis of magnetic microspheres and the development of new macro-micro hierarchically porous magnetic framework composites

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Statement of contribution

- Woodliffe J. L.: literature review/research, laboratory experiments, analysis and characterisation, creation of figures/graphs/tables, writing original draft, review & editing, topic conceptualisation
- Molinar-Díaz J.: analysis (MLA), review & editing
- Islam M. T.: contribution to PMM synthesis methodology, review & editing
- Stevens L. A.: analysis (Kr gas sorption), creation of graphs (Kr gas sorption), review and editing (Kr gas sorption, MIP)
- Wadge M. D.: analysis (XPS), writing original draft (XPS), creation of figures and tables (XPS), review & editing
- Rance G. A.: analysis (Raman), writing original draft (Raman), creation of figures (Raman SI figures), review & editing
- Ferrari B.: review & editing, topic conceptualisation
- Ahmed I.: review & editing, topic conceptualisation
- Laybourn A.: review & editing, topic conceptualisation

Rapid synthesis of magnetic microspheres and the development of new macro-micro hierarchically porous magnetic framework composites

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Abstract

Magnetic framework composites (MFCs) are a highly interesting group of materials that contain both metal-organic frameworks (MOFs) and magnetic materials. Combining the unique benefits of MOFs (tuneable natures, high surface areas) with the advantages of magnetism (ease of separation and detection, release of guests by induction heating), MFCs have become an attractive area of research with many promising applications. This work describes the rapid, scalable synthesis of highly porous magnetic microspheres via a flame-spheroidisation method, producing spheres with particle and pore diameters of $206 \pm 38 \mu\text{m}$ and $12.4 \pm 13.4 \mu\text{m}$, respectively, with a very high intraparticle porosity of 95%. The MFCs produced contained three main iron/calcium oxide crystal phases and showed strong magnetisation (M_s : 25 emu/g) and induction heating capabilities ($\approx 80^\circ\text{C}$ rise over 30 s at 120 W). The microspheres were subsequently surface functionalised with molecular and polymeric coatings (0.7-1.2 wt.% loading) to provide a platform for the growth of MOFs HKUST-1 and SIFSIX-3-Cu (10-11 wt.% loading, 36-61 wt.% surface coverage), producing macro-micro hierarchically porous MFCs (pores $>1 \mu\text{m}$ and $<10 \text{ nm}$). To the best of our knowledge, these are the first example of MFCs using a single-material porous magnetic scaffold. The adaptability of our synthetic approach to novel MFCs is applicable to a variety of different MOFs, providing a route to a wide range of possible MOF-microsphere combinations with diverse properties and subsequent applications.

1 Introduction

Magnetic framework composites (MFCs) are an exciting group of materials comprising both metal-organic frameworks (MOFs) and magnetic materials¹. MOFs are porous coordination polymers containing metal ions or clusters as nodes, and linkers consisting of organic molecules². Their tuneable natures and high internal surface areas (up to 7800 m²/g)³ have enabled them to be explored for applications across a wide range of fields, including gas storage and separation^{4,5}, chemical sensing⁶, biomedicine⁷ and many more^{8,9}. Sustainability and circularity considerations for MOFs are also currently advancing^{10–12}. By combining these unique benefits and applications with the advantages of magnetism, the resulting MFCs have become a highly attractive area of research¹³. One such example is in the development of materials to capture carbon dioxide from flue gas. Hill *et al.* showed that attaching MOFs, such as Mg-MOF-74 or UiO-66, to magnetic nanoparticles provides an energy-efficient method to desorb captured CO₂ from within the saturated MOF using rapid, localised magnetic induction heating¹⁴. Another example is from Yan *et al.* who used MIL-101(Cr) with functionalised magnetic microparticles for the magnetic solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples¹⁵. Further applications of MFCs in environmental remediation, adsorption, sensing, biomedicine and catalysis, alongside preparation strategies for forming these composites are discussed at length in the literature^{1,16–18}.

Previous development work with MFCs has almost entirely been focused on nanosized iron oxides as the magnetic components¹, likely due to the high magnetisation and abundance of iron, and the ease of manufacture of the nanoparticles. This work, therefore, also starts with an iron oxide (magnetite), but describes an investigation into the single-stage synthesis of micro-sized low and high porosity magnetic microspheres (ranging from 50 – 300 µm in diameter). These are synthesised via a rapid, cost-effective and scalable flame-spheroidisation process, building on our recent work^{19,20}. These microspheres not only avoid the safety concerns over the use of nanoparticles^{21,22}, but also offer additional advantages over

their nano-alternatives such as: improved flow properties/no particle agglomeration, beneficial for powder handling and scale-up; more sustainable synthesis route; increased ease of magnetic separation due to size^{23,24}; the potential to avoid the need for granulation/pelletisation in industrial applications; and the potential to form hierarchal porosity when combined with other porous materials such as MOFs, demonstrated to benefit many applications such as adsorption, separation and catalysis^{25–27}.

Apart from their use in MFCs, magnetic micro- and nano-particles have also found various applications from biomedicine²⁸ and catalysis^{13,29} to environmental remediation³⁰. Their advantages often come from their ease of detection, efficient separation by magnetic fields and induction heating capability^{31,32}. In addition to the magnetic properties, imparting porosity into the particles offers additional benefits due to the high surface areas and low densities produced, which can also enhance performance in applications involving the encapsulation of a substance, such as in drug delivery³³ or separation/removal of molecules or heavy metals^{34,35}. These magnetic particles are typically surface functionalised to enhance interactions with other molecules and facilitate the formation of composite materials³⁶. One frequent route is using self-assembled monolayers such as mercaptoacetic acid³⁷, mercaptopyridine (MPYR)³⁸, amino alkoxysilanes³⁹ or tetraethyl orthosilicate⁴⁰. These routes affix functional groups such as -COOH or -NH₂ to the surface of the particles, allowing them to form strong chemical bonds with other molecules during the formation of composites. Other common functionalisation agents are polymers, such as polydopamine (PDA)⁴¹, polyethylenimine⁴², polystyrene sulfonate⁴³, polyvinylalcohol (PVA)⁴⁴ and polyvinylpyrrolidone⁴⁵. These can adhere to the particles and act as binders for further composite development.

Alongside synthesis and optimisation studies of the highly porous magnetic microspheres (PMMs) made from iron and calcium oxides, we also describe their composition and morphology, induction heating capabilities and magnetisation, comparing to low porosity counterparts. Surface functionalisation of the PMMs with PDA and MPYR was then conducted. Finally, the formation of novel macro-micro hierarchically porous MFCs (pores >1 μm and <10 nm) with these PMMs and

archetypal MOF HKUST-1⁴⁶ and innovative carbon-capture MOF SIFSIX-3-Cu⁴⁷ was demonstrated. To the best of our knowledge, these represent the first examples of MFCs using a single-material porous magnetic scaffold. A schematic representation of this process is shown in Figure 1. These initial results with different MOFs highlight the potential suitability of the MFCs for a range of applications.

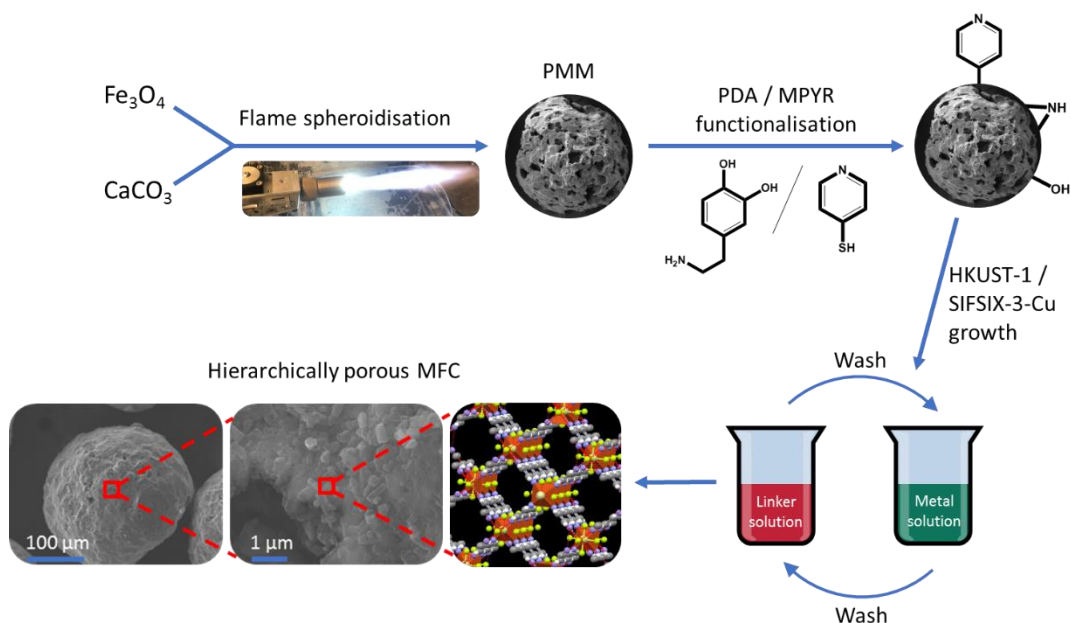


Figure 1. Schematic illustration of the synthesis procedure for the macro-micro hierarchically porous magnetic framework composites.

2 Experimental section

2.1 Materials

All chemicals and reagents were used as received. Fe₃O₄ was obtained from Inoxia; CaCO₃ was purchased from Longcliffe. Dopamine hydrochloride, tris(hydroxymethyl)aminomethane (≥99.8%), copper(II) acetate monohydrate (ACS reagent, ≥98%), 4-mercaptopyridine (95%), pyrazine (≥99%) and trimesic acid (95%) were bought from Sigma Aldrich, UK. Copper hexafluorosilicate hydrate was acquired from Fluorochem Ltd. Methanol (≥99.9%) was purchased from Fisher Scientific. Acetic acid (glacial) was obtained from VWR Chemicals. Polyvinyl alcohol (87.0-89.0% hydrolysed, M.W ≈ 13,000-23,000) was purchased from Acros Organics. Ethanol

(absolute, SpS grade) was purchased from Scientific Laboratory Supplies Ltd.; all water used was deionised.

2.2 Preparation of pristine iron/calcium oxide magnetic microspheres

Synthesis of pristine highly porous magnetic microspheres (PMMs). Fe_3O_4 (10 g, 0.04 mol, particle size: $<45\ \mu\text{m}$) was mixed with CaCO_3 (5 g, 0.05 mol, particle size: $<45\ \mu\text{m}$) in a 2:1 mass ratio. The mixture was ground using a ball mill for 5 minutes at 500 RPM (Retsch PM100) and then granulated with the addition of PVA (2 wt.% solution in deionised water) dropwise in a pestle and mortar. Once larger granules had formed, the mixture was sieved and granular particles between 125 and 212 μm were set aside for flame spheroidisation. Granules above 212 μm were ground further, whilst particles less than 125 μm were re-granulated to maximise the yield of particles between 125 and 212 μm . This process was again repeated until most of the starting material had been utilised. The total quantity of PVA added throughout was 4.0 mL. The set-aside granular particles were again sieved one last time, and those $>125\ \mu\text{m}$ were spheroidised using a thermal flame spray gun (MK74, Metallisation Ltd, UK) with an oxy-acetylene gas flow ($\text{C}_2\text{H}_2:\text{O}_2$ 1:1). The microsphere products were collected, acid washed with acetic acid (5 M (aq), 1 minute), filtered (63 μm mesh) and rinsed extensively with deionised water before drying in an oven overnight (50 °C). The dry samples were then sieved into two fractions ($>125\ \mu\text{m}$ and $<125\ \mu\text{m}$). Microspheres $>125\ \mu\text{m}$ ($\approx 60\%$ of total microspheres produced) were taken as the final product. These microspheres were then stored in glass vials for analysis and further use.

Synthesis of pristine low porosity magnetic microspheres. Followed same process as above, without the addition of any CaCO_3 or size fractioning.

2.3 Functionalisation of porous microsphere surfaces

Polydopamine (PDA). Dopamine hydrochloride (200 mg, 1.05 mmol) was dissolved in tris buffer (100 mL, 10 mM, pH 8.5) in a glass dish. 0.5 g of PMMs were added, and the solution agitated overnight on a shaker plate (17 h). PDA functionalised PMMs

were collected by magnetic separation with a bar magnet and washed with water (100 mL x 3) before drying in an oven (50 °C, >4 h).

Mercaptopyridine (MPYR). 4-Mercaptopyridine (56 mg, 0.50 mmol) was mixed in ethanol (abs., 50 mL) in a glass dish. 0.15 g PDA functionalised PMMs were added, and the solution agitated on a shaker plate (5 h). PDA/MPYR functionalised PMMs were collected by magnetic separation with a bar magnet and washed with ethanol (25 mL x 2) before drying in an oven (50 °C, >4 h).

2.4 Synthesis of magnetic framework composites (MFCs)

HKUST-1@PMM (PDA) MFC. Layer-by-layer method: Cu(OAc)₂·H₂O in EtOH (2.5 mL, 100 mM) and trimesic acid in EtOH (2.5 mL, 100 mM) solutions were prepared. 0.05 g of PDA functionalised PMMs were added to the Cu(II) salt solution for 15 mins, separated using a magnet, washed with EtOH (1 mL), and dried under an N₂ stream. The PMMs were then added to the trimesic acid solution for 30 mins, separated using a magnet, washed with EtOH (1 mL), and dried under an N₂ stream. This process was repeated for 10 cycles before combining the Cu(II) salt and trimesic acid solutions with the PMMs and heating the solution to 50 °C for two days. Finally, HKUST-1@PMM (PDA) MFC product was collected by magnetic separation, washed with EtOH, dried briefly under an N₂ stream and then in a vacuum oven at 100 °C (>2 h).

SIFSIX-3-Cu@PMM (PDA). Layer-by-layer method: CuSiF₆·H₂O in MeOH (2.5 mL, 290 mM) and pyrazine in MeOH (2.5 mL, 750 mM) solutions were prepared. 0.03-0.05 g PDA functionalised PMMs were added to the Cu(II) salt solution for 15 mins, separated using a magnet, washed with MeOH (2.5 mL), and dried under an N₂ stream. The PMMs were then added to the pyrazine solution for 15 mins, separated using a magnet, washed with MeOH (2.5 mL), and dried under an N₂ stream. This process was repeated for 8 cycles then the microspheres were left in the final pyrazine solution for 24 h. Finally, SIFSIX-3-Cu@PMM (PDA) MFC product was collected by magnetic separation, washed with MeOH and dried in an oven at 50 °C.

SIFSIX-3-Cu@PMM (PDA/MPR). Same process to above, except using PDA/MPYR functionalised PMMs.

2.5 Characterisation

X-ray diffraction. X-ray diffraction patterns of the microspheres, MOFs, and composites were obtained using a Bruker D8 Advance DaVinci, Lynxeye 1D detector, motorised air scatter screen, Cu K α radiation ($\lambda = 0.15418$ nm), operating at 40 kV and 40 mA in Bragg-Brentano geometry. Pattern matching and semi-quantitative analysis of constituents were performed with Bruker DIFFRAC.EVA (ver. 6.0.0.7) software and powder diffraction files from the databases.

Scanning electron microscopy. SEM images of the microspheres were taken on a JEOL JSM-6490, using an acceleration voltage of 15 kV, taking secondary electron images with a working distance of 10 mm. A spot size of 45 was used, and samples were held on Al stubs and platinum coated. Microsphere size distributions were calculated using Fiji ImageJ software⁴⁸. Cross sectioned samples were obtained by embedding the microspheres in cold epoxy resin followed by grinding, polishing and carbon coating. Elemental composition analyses of microsphere cross sections were performed by mineral liberation analysis (MLA) (FEI Quanta600 MLA, 20 kV; spot size 7) with energy dispersive X-ray spectroscopy (EDS) and computer software (FEI Quanta600 MLA, Bruker/JKTech/FEI software) for data acquisition for automated mineralogy. SEM images and EDS elemental analyses of the MFCs were taken on a JEOL 7000F FEG-SEM, acceleration voltage 15 kV, secondary electron images, working distance 10-11.5 mm, iridium/carbon coating.

X-ray photoelectron spectroscopy. XPS analyses were performed using a VG Scientific EscaLab Mark II with an Al K α monochromatic X-Ray Source. Scans were collected at: 20 mA and 12 kV emissions; angle of incidence ca. 30 °; step size 1 eV (survey), 0.2 eV (high-res); replicate scans = 2 (survey), 5 (high-res); dwell time 0.2 s/step (survey), 0.4 s/step (high-res). Charge correction calibration was conducted at 284.8 eV for the C 1s peak. Spectra analyses and peak fitting were performed using

CasaXPS software⁴⁹, using a Shirley background subtraction. The Full Width at Half Maximum (FWHM) was constrained for all convolutions of the same element.

Infra-red spectroscopy. FT-IR spectra were recorded on a Bruker IFS66 with KBr beamsplitter, Globar light source, DTGS room temperature detector and Specac “Goldengate Bridge” diamond ATR attachment. The instrument was air purged using a Parker Balston 75-52 FT-IR Purge Gas Generator.

Confocal Raman microscopy. Raman spectra and images were collected using a HORIBA LabRAM HR Raman microscope equipped with a 532 nm laser (~5 mW power). To simultaneously scan a range of Raman shifts, a 300 lines mm⁻¹ rotatable diffraction grating along a path length of 800 mm was employed. Spectra were detected using a Synapse CCD detector (1024 pixels) thermoelectrically cooled to -60 °C. Before spectra collection, the instrument was calibrated using the zero-order line and a standard Si (100) reference band at 520.7 cm⁻¹. The spectral resolution in this configuration is ~3.7 cm⁻¹. For single point measurements, spectra were acquired over the range 100-3100 cm⁻¹ with an acquisition time of 120-150 seconds and 4 accumulations, to automatically remove the spikes due to cosmic rays and improve the signal to noise ratio, and using a 100x objective and a 50 µm confocal pinhole to enhance confocality. Spectra were collected from at least three locations and averaged to give a mean spectrum. For Raman imaging, spectra were acquired at 5 µm intervals from an area 400x400 µm (6,561 spectra), using a 50x objective and 300 µm confocal pinhole. Autofocussing at each position was performed using the Mosaic and ViewSharp™ imaging modules within Labspec 6.5 software. As each individual spectrum was collected for 5 seconds, repeated once, each map required approximately 20 hours of acquisition time. The intensity (as height) of bands diagnostic of either HKUST-1 (960-1060 cm⁻¹, blue) or SIFSIX-3-Cu (990-1100 cm⁻¹, green) and polydopamine (1100-1800 cm⁻¹, red) was evaluated within the respective maps of PMM@HKUST-1 and PMM@SIFSIX-3-Cu using univariate analysis.

Kr gas sorption. Krypton (Kr) gas sorption isotherms were carried out using a Micromeritics ASAP 2420 (Micromeritics, Norcross, GA, USA) at -196 °C. Approximately 50 mg samples were degassed under vacuum at 105 °C for 15 hours

before analysis to remove moisture and other adsorbed gases. Kr gas, 99.995%, was further purified by sublimation under reduced pressure at -196 °C before analysis. Due to the solidification of krypton at higher pressures at -196 °C, sorption isotherms were carried out from 0.10 to 0.65 relative pressure. The microsphere isotherms were subtracted from the microsphere + MOF isotherms, and the weight was corrected to give an accurate sample weight of the deposited MOF, generating an isotherm solely for the MOF. The specific surface area was acquired from 0.05-0.30 relative pressure using the BET model, and pore volume/size distribution (1.75-20 nm) from an extension of the BJH model by Chao et al.⁵⁰ using Microactive V5.0 (Micromeritics, Norcross, GA, USA).

Thermogravimetric analysis (TGA). TGA was carried out using a TGA550 Discovery (TA Instruments) with an automated vertical overhead thermobalance. 5-20 mg of sample was heated at a rate of 10 °C/min under an N₂ atmosphere (1 bar, 60 mL/min).

Vibrating-sample magnetometry. Magnetometry measurements were taken using 50-125 mg of sample on a SQUID MPMS3 (Quantum Design) at the University of Sheffield via the Royce Institute. Measurements were taken at room temperature with a field strength up to 10 kOe.

Mercury intrusion porosimetry. The porosity and pore diameters of the high and low porosity microspheres were determined via mercury intrusion porosimetry using a Quantachrome Poremaster Porosimeter at the SAXS/CNIE Facility in the Chemical Engineering Department at UCL. Samples were placed in a 0.5 cm³ penetrometer with 2 mm inner diameter and placed under vacuum. Mercury was initially intruded into the cell under pressure ranging from 0.85 to 50 psia. Samples were then transferred to a high-pressure station where mercury intrusion took place at pressures ranging from 20 to 30,000 psia. The corresponding pore diameter range (210 µm to 6 nm) was calculated using the Washburn Equation⁵¹ with a mercury surface tension of 480 mN/m and a contact angle of 130° (intrusion and extrusion). Bulk sample density was calculated at 9.39 psi for the low porosity microspheres and 2.21 psi for the high porosity microspheres, corresponding to the size of the largest

pores by SEM (28 and 80 μm , respectively). Skeletal density was measured using a Quantachrome Pentapyc 5200e gas pycnometer, using helium as the intrusion gas at a pressure of 19.0 psig. Porosity (%) was calculated using the bulk and skeletal densities.

2.6 Induction heating

Induction heating measurements were undertaken using a 2 kW induction heater (204 kHz, Cheltenham Induction Heating Ltd.) and the temperature measured with a fibre optic thermocouple (Neoptix Reflex). The thermocouple was placed in a borosilicate glass tube (internal diameter: 11 mm) with 2.4 g of sample powder. The tube was then placed in a water-cooled copper coil (internal diameter: 27 mm, height: 38 mm) and various voltage settings were used to apply power to the sample. All measurements were recorded in triplicate, plotting averages with error bars showing ± 1 standard deviation.

3 Results and discussion

3.1 Synthesis and characterisation of magnetic microspheres

Highly porous magnetic microspheres (PMMs) were synthesised using a rapid and scalable flame spheroidisation process, expanding on previous work²⁰. PMMs have potential use in a variety of applications as previously discussed, including herein as scaffolds for further surface growth of MOFs in the production of MFCs with hierarchical porosity. During the optimisation process, parameters such as flame collection distance, starting material ratios, particle sizes, grinding durations and methods (puck and ring mill, ball mill) were investigated. The variable with the largest effect on porosity was found to be grinding of Fe_3O_4 with CaCO_3 prior to flame processing, which was optimised at 5 min in a ball mill, as detailed in the experimental section. Grinding has a significant effect as CaCO_3 must be well mixed within the starting Fe_3O_4 granules during melting and decomposition to allow CO_2 to form pores as it escapes while the microspheres cool and solidify. Without this level of mixing, CO_2 can escape without leaving pores behind in the cooling microspheres.

Less vigorous mixing techniques resulted in a decreased porosity (Figure S1, Supplementary Information). Low porosity solid microspheres were also produced using a similar process without porogen, with potential for use in applications where porosity is not required (e.g. in the production of core-shell composites for biocatalysis⁵²), as well as for property comparisons with the high porosity microspheres.

SEM micrographs of the high and low porosity microspheres and their cross-sections are shown in Figure 2. The low porosity microspheres (Figure 2 'A') show a high degree of shape and size uniformity, with solid fillings shown in the cross-sections (Figure 2 'B'). The high porosity microspheres (Figure 2 'C') also show reasonable uniformity, with external pores opening to internal cavities. As shown in the cross-sectional image of the high porosity microspheres (Figure 2 'D'), some microspheres have pores which are large enough that the viscous resin used for embedding has entered the spheres (labelled 'R'), and others where the pores are too small for the resin to enter (labelled 'E'). It is considered that the microspheres are formed by the melting of the starting material granules in the flame ($\approx 3100^\circ\text{C}$)⁵³, leading to droplet formation, followed by rapid cooling and solidification as they are ejected from the flame²⁰. The spherical shape is the result of minimising surface tension, and porosity is suggested to arise from the decomposition of the porogen material releasing CO_2 gas, which is trapped in the molten particles and escapes during the cooling and solidification stage. The pore size distribution of the high porosity microspheres was first determined using ImageJ software measuring 268 pores (see Figure S2, Supplementary Information). The average microsphere was found to have approximately 45 pores, with a mean pore diameter of $12.4\ \mu\text{m}$ and a standard deviation of $13.4\ \mu\text{m}$, demonstrating macro-porosity. Porosity was further quantified through mercury intrusion porosimetry analysis on both the high and low porosity microspheres⁵¹. Figure 3 'C' shows the decreasing pore diameters (from increasing mercury pressure) plotted against the cumulative volume of mercury intrusion (pore volume). The initial increase in gradient for both samples (point 'X') is from the filling of the interparticulate gaps/voids between the microspheres⁵⁴. The high porosity microspheres also exhibit a change in gradient (point 'Y') as a new size range of

intraparticulate pores are filled⁵⁴. Figure 3 'D' plots the pore diameter against the negative log differential volume intrusion for the high and low porosity microspheres up to the interparticle filling limits. These data correspond well to pore size distributions measured by analyses of SEM images (Figure S2, Supplementary Information). Intraparticle porosity was calculated as follows (eq 1)⁵⁵:

$$\text{Intraparticle porosity (\%)} = 100 \left[1 - \frac{\rho_{Hg}}{\rho_{He}} \right] \quad (1)$$

Where ρ_{Hg} is the bulk density by low-pressure mercury intrusion, and ρ_{He} is the skeletal density by helium intrusion. The low porosity microspheres demonstrated an intraparticle porosity of 52%, and the high porosity microspheres an intraparticle porosity of 95%, thus quantifying the increase in porosity caused by the inclusion of CaCO_3 with the Fe_3O_4 in the flame spheroidisation process. Similar low porosities (35-47%) have been observed by mercury intrusion in the formation of porous hydroxyapatite biomaterials for other applications (using CaCO_3)⁵⁶. Porous magnetic microspheres reported by Tai *et al.* demonstrated porosities of 4-24%⁵⁷ by mercury intrusion, synthesised via a 5 h suspension polymerisation with a magnetic fluid, requiring multiple reaction steps with inert atmospheres and organic solvents⁵⁷. These highlight the benefits of our procedure, able to produce magnetic microspheres with very high intraparticle porosities in a rapid and solvent-free synthesis.

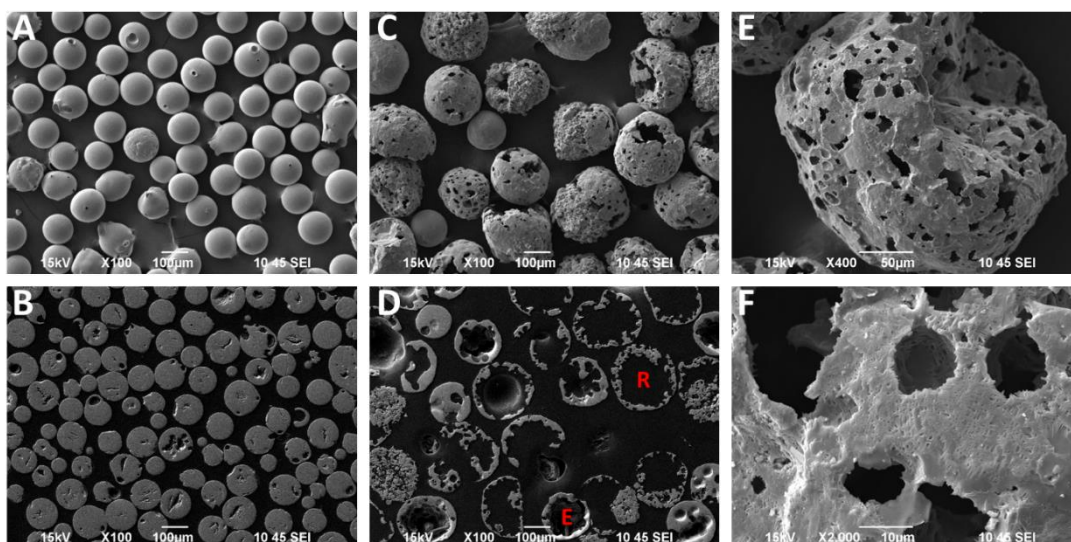


Figure 2. SEM micrographs of: A, low porosity microspheres; B, cross section of low porosity microspheres; C, high porosity microspheres; D, cross section of high porosity microspheres, showing both resin filled (R) and empty (E) examples; E, singular high porosity microsphere; F, image of a high porosity microsphere at higher magnification.

The production yields of the spheroidisation and acid washing steps for the high and low porosity microspheres synthesised herein are shown in Table 1. Spheroidisation yield was calculated as the mass of microspheres produced (prior to sieving for the high porosity microspheres) divided by the mass of the granulated starting materials. Higher spheroidisation yields were observed with the low porosity microspheres, likely due to the mass loss of CO_2 from the CaCO_3 porogen used to generate pores in the high porosity microspheres²⁰. Other mass losses include particles missing the centre of the flame or falling outside of the collection trays. It was also observed that acid washing caused no mass loss for the low porosity microspheres, and a negligible loss for the high porosity microspheres, likely from the dissolution of any unreacted CaCO_3 porogen. Image particle size analyses of the high and low porosity microspheres (N= 114 and 143, respectively) are also shown in Table 1. The larger sizes of the high porosity microspheres are evidence of the expanding process of the particles in the flame during synthesis, where porogen decomposition leads to CO_2 gas release (generating pores). The higher size range and standard deviation of the high compared to the low porosity microspheres likely arises from slight variation in the exact amount of porogen present in each particle due to the granulation method.

Table 1. Particle sizing from image analysis and yields of the spheroidization and acid washing steps for high and low porosity microspheres. Spheroidization yield was calculated as the mass of microspheres produced over the mass of the granulated starting materials.

	High porosity microspheres	Low porosity microspheres
Spheroidization yield (%)	76	84
Acid washing yield (%)	98	100
Size range (µm)	120-285	73-194
Average size (µm)	206	134
Standard deviation (µm)	38	24

To determine the crystalline mineral phases present, the high and low porosity microspheres were analysed using powder X-ray diffraction. As shown in Figure 3 'A', the low porosity microspheres exhibited a peak pattern corresponding to a cubic magnetite phase (Fe_3O_4 : PDF 00-019-0629), as identified from the DIFFRAC.EVA powder diffraction file database. The high porosity microspheres exhibited a pattern containing peaks corresponding to a cubic magnetite phase and two main calcium iron oxide phases, identified from the database and marked in Figure 3 'A' as Fe Ca oxide A and B (A: PDF-01-071-2108; B: PDF-00-013-0395). 'Oxide A' corresponds to the known orthorhombic structure Srebrodolskite ($\text{Ca}_2\text{Fe}_2\text{O}_5$), whereas 'oxide B' is a more complex calcium iron oxide with a rhombohedral lattice. In order to quantify the mineral compositions present and obtain a better understanding of the chemical properties of the materials, a detailed compositional analysis of both the high and low porosity microspheres was undertaken using mineral liberation analysis (MLA). Figure 3 'B' shows a breakdown of the minerals present in the samples. Different minerals are colour-coded and their elemental compositions were determined via EDS analysis, as shown in the formulae on the right-hand side of the figure. The low porosity microspheres are composed entirely of Fe_3O_4 , suggesting that no oxidation to Fe_2O_3 or higher oxides takes place during the flame process, corroborating the PXRD data. The high porosity microspheres are mainly composed of two calcium iron oxide mineral compositions with Fe to Ca ratios of 2:1 and 3:1, though some other mineral compositions with higher ratios of Fe are also present. Table 2 shows the percentage by weight of the different mineral compositions present in the high

porosity microspheres. EDS analyses show bands of locally averaged compositions, likely from multiple mineral phases. Assessment using the three-phase diagram for Ca-Fe-O on the highest wt.% mineral compositions ($\text{Fe}_{2.98}\text{Ca}_{1.02}\text{O}_4$ and $\text{Fe}_{2.73}\text{Ca}_{1.27}\text{O}_4$) showed that the $\text{Ca}_2\text{Fe}_2\text{O}_5$ phase (Fe Ca oxide A) was thermodynamically favoured, consistent with the PXRD pattern⁵⁸. The other expected thermodynamic phase was a Wustite-Lime solid solution containing iron and calcium oxides. This phase may represent the Fe Ca oxide B shown in the PXRD pattern (Figure 3 'A'), or the rapid cooling of the flame process could have resulted in the formation of a complex metastable calcium iron oxide phase.

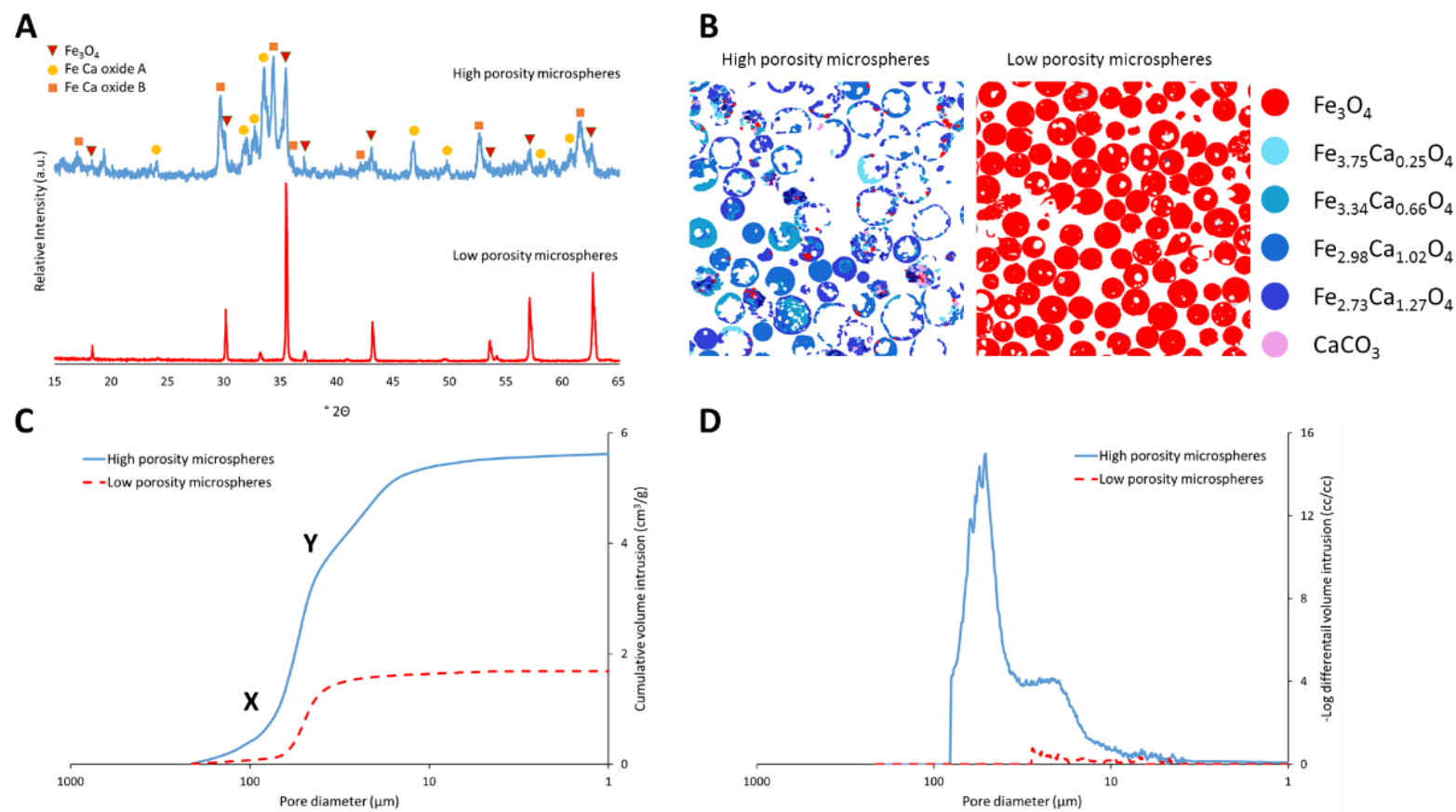


Figure 3. A, powder X-ray diffraction patterns for high (top) and low (bottom) porosity microspheres. B, MLA images showing mineral mapping cross-sections of high (left) and low (right) porosity microspheres. Mineral phases are colour coded and their elemental compositions are shown in the figure legend (far right). C, mercury intrusion porosimetry data showing pore diameter against cumulative volume intrusion (pore volume) for the high and low porosity microspheres. Point 'X' shows the filling of interparticle voids, and point 'Y' shows a change in gradient as a new range of pore sizes are filled. D, mercury intrusion porosimetry data showing pore diameter against the -log differential volume intrusion for the high and low porosity microspheres up to the interparticle filling limits.

Table 2. Mineral phases present in the high porosity microspheres, alongside their Fe/Ca molar ratios and weight percentages as determined by MLA and EDS.

Mineral	Fe/Ca molar ratio	High porosity microspheres (wt. %)
Fe₃O₄	-	4.2
Fe_{3.75}Ca_{0.25}O₄	15	4.4
Fe_{3.34}Ca_{0.66}O₄	5	9.7
Fe_{2.98}Ca_{1.02}O₄	3	35.3
Fe_{2.73}Ca_{1.27}O₄	2	44.4
CaCO₃	-	0.7

3.2 Magnetisation and induction heating of microspheres

The magnetic properties of the microspheres at room temperature were measured and compared to the pure magnetite starting material by vibrating sample magnetometry (VSM), see Figure 4 ‘A’. All samples showed ferrimagnetic behaviour with low remnant magnetisation (<1.1 emu/g) and intrinsic coercivity (<50 Oe), resulting in high permeability and low energy required to switch the spin directions. This result is beneficial for applications involving magnetic separation such as in environmental remediation, where only low energies would be required to magnetise the microspheres for collection, and they could also be easily demagnetised and re-dispersed by the removal of the magnetic field. The saturation magnetisation (M_s) values for the pure magnetite starting material, and the low and high porosity microspheres were 94, 91 and 25 emu/g, respectively (Figure 4 ‘A’). The similarity of the magnetisation curve of low porosity microspheres to pure magnetite showed that there were no significant structural changes induced during flame spheroidization that would result in a decrease of M_s . The low porosity microspheres high M_s value of 91 emu/g is significant, with values between 75 and 90 emu/g for processed magnetite commonly noted for being “high” in the literature^{59–61}. The drop in M_s for high porosity magnetite was expected due to the introduction of non-magnetic calcite, resulting in the production of less magnetic mineral phases such as

$\text{Ca}_2\text{Fe}_2\text{O}_5$ ⁶², as shown in the XRD and MLA data in Figure 3. However, an M_s value of 25 emu/g was still sufficiently high for the microspheres to exhibit strong magnetic behaviour and benefits, as shown by the induction heating study below.

Induction heating is the process of energy deposition from an H-field applicator to a material placed in the magnetic field node. In conductive materials, heating occurs through ohmic losses from the resistance to induced eddy currents. In ferromagnetic materials, heating is additionally caused by magnetic hysteresis, an effect associated with losses from the magnetization-demagnetization cycle in magnetic domains⁶³. As discussed in the introduction, the ability of magnetic microspheres to undergo induction heating is beneficial to many applications; for example, in the release of adsorbed or encapsulated guests or in medical treatments such as hyperthermia⁶⁴. Therefore, the induction heating ability of the high and low porosity magnetic microspheres were investigated and compared to the magnetite and calcite starting materials. Rapid heating was indeed observed for the microspheres, confirming their potential usefulness in such applications. Figure 4 'B' shows the change in temperature over 30 seconds at 120 W (applied magnetic field of 100 A/m) for the high and low porosity microspheres, alongside the magnetite and porogen starting materials. As expected, calcite showed negligible heating under a magnetic field (0.4 ± 0.7 °C rise over 30 seconds), whilst pure magnetite powder heated very rapidly (116 ± 25 °C rise over 20 seconds). Interestingly, the high and low porosity microspheres exhibited similar heating profiles (81 ± 3 °C cf. 80 ± 7 °C rise over 30 seconds, respectively) (Figure 4 'B'), despite their differences in composition and magnetic susceptibility (Figure 4 'A'). We hypothesise that this effect could be due to the size and shape of the high and low porosity processed microspheres compared to the magnetite starting material. Both sets of microspheres have large spherical morphologies, resulting in low contact areas between particles and with the thermocouple in the sample tube. This low contact may limit the transfer of heat between neighbouring particles and to the fibre-optic thermocouple. This limit may be similar for both high and low porosity microspheres as both show similar spherical morphologies compared to the fine and dense powder magnetite starting material (<45 μm). For industrial applications, both energy and time must be balanced to

achieve efficient heating. As such, we also briefly explored the effect of varying the power from the induction heater, where the high porosity microspheres were subjected to three different power levels from 30 W (applied magnetic field of 75 A/m) to 250 W (applied magnetic field of 125 A/m), each for 30 seconds. The results are shown in Figure 4 'C'. As anticipated, increasing the power resulted in a faster heating rate. However, the increase was not directly proportional to the input power due to the complex nature of the many factors affecting the heating mechanisms, including applicator efficiency⁶³. Figure 4 'C' shows that reasonable heating rates can be achieved with even very low power (31 ± 2 °C rise over 30 seconds at 30 W), whereas increasing the power by over a factor of two from 120 to 250 W only increased the heating rate from an 81 ± 3 °C to a 102 ± 3 °C rise over 30 s.

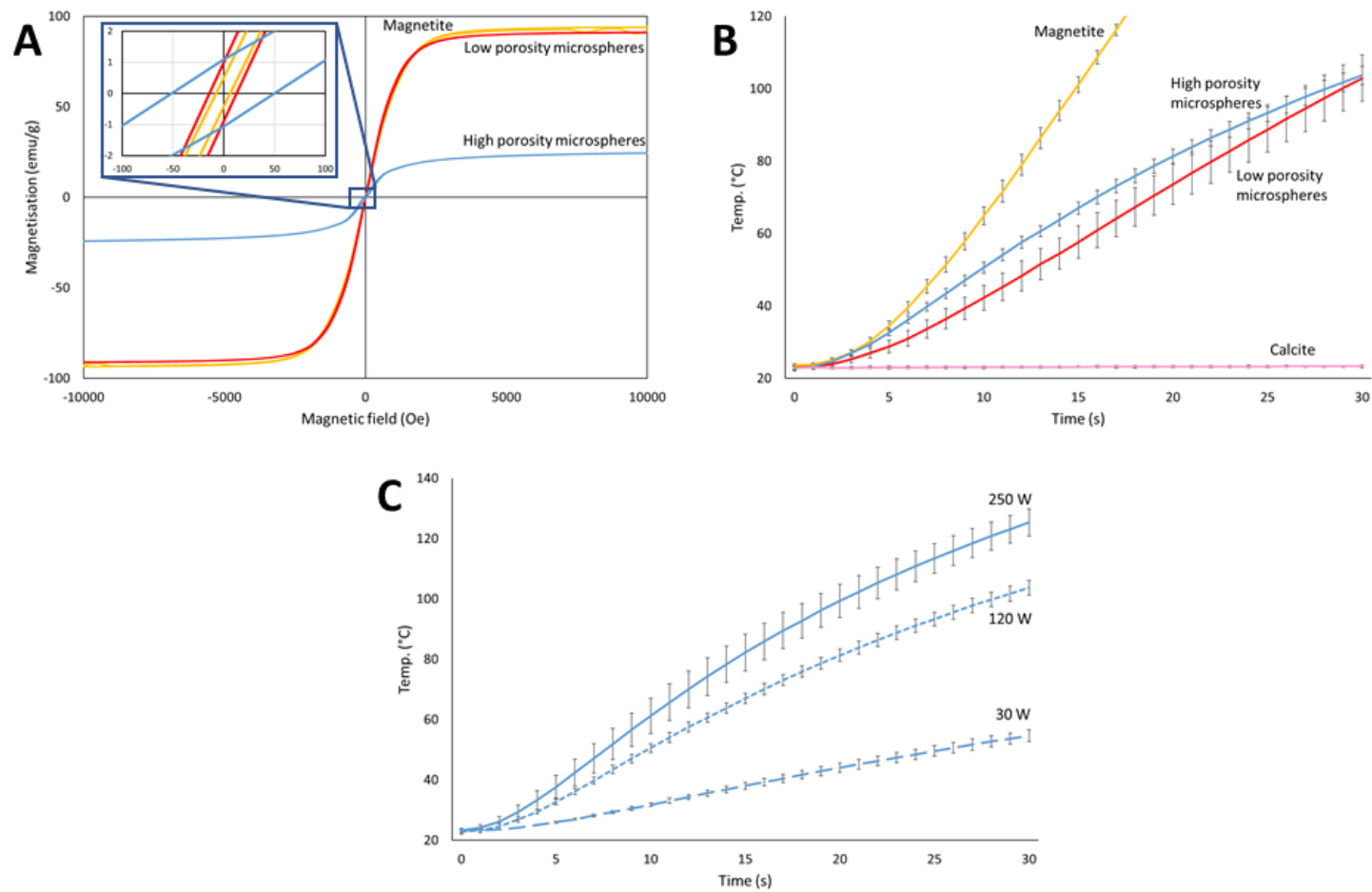


Figure 4. Plots showing: A, Room-temperature magnetisation curves of high (blue) and low (red) porosity microspheres alongside the pure magnetite starting material (yellow); B, induction heating rate of high (blue) and low (red) porosity microspheres alongside magnetite (yellow) and calcite (pink) starting materials at 120 W; C, induction heating rate of high porosity microspheres at 30 W, 120 W and 250 W. Measurements in B and C were taken in triplicate and the averages plotted, the error bars show ± 1 standard deviation.

3.3 Functionalisation of highly porous magnetic microspheres

Having compared the properties of high and low porosity magnetic microspheres, subsequent efforts focused on the highly porous magnetic microspheres (PMMs) due to the potential benefits of porosity such as high surface areas, low densities, and guest encapsulation capabilities as described in the introduction. Firstly PDA was used as a surface functionalisation agent to coat the PMMs prior to MOF growth, due to literature precedent^{65,66}. PDA contains a mixture of catechol, quinone, amine and imine functional groups, which can provide good binding sites for composite formation. We further trialled MPYR on PDA⁶⁵ for SIFSIX-3-Cu MFC, as the pendant pyridine functional group of MPYR was expected to have good compatibility with the MOF (which contains pyrazine linkers).

The presence of PDA and MPYR on the PMMs was investigated using detailed XPS analyses. Figure 5 shows the high-resolution spectra for the pristine PMMs alongside the surface functionalised PMMs. More detailed classifications and analyses can be found alongside the XPS survey spectra in Figure S4, Supplementary Information. XPS data of the pristine PMMs evidence metallic-bound oxygen in the O 1s spectrum at 530.2 eV and the expected Fe(III) and Ca(II) peaks in the Fe 2p and Ca 2p spectra, at 710.8 eV and 346.5 eV, respectively for the 3/2 peaks. The PDA and PDA/MPYR functionalised PMMs both show the anticipated nitrogen peak in the N 1s spectrum at 399.5 eV, corresponding to the polydopamine layer^{67,68}. Evidence of C—N is also seen in the C 1s deconvolution at 285.7 eV, and the O 1s spectrum shows the C=O and C—O peaks expected from the quinone and catechol moieties in polydopamine, at 288.8 eV and 286.9 eV respectively⁶⁹. Both the iron and calcium peaks are missing in these samples, indicating that the polydopamine layer must be thicker than the penetration depth of the XPS analysis technique, around 10 nm⁷⁰. Finally, a low intensity S 2p peak at 163.3 eV in the PDA/MPYR functionalised sample confirms the presence of the MPYR on the PDA layer on the PMMs. MPYR is possibly attached by a reaction between the terminal thiol on MPYR and the catechol/quinone groups of the polydopamine, through a thiol-nucleophile Michael addition type reaction^{65,71,72}.

Quantities of the functionalisation agents on the surfaces of the PMMs were determined by thermal gravimetric analyses, analysing the weight loss from decomposition of the organic agents on the inorganic PMMs (Figure S3, Supplementary Information). PDA functionalised PMMs showed a weight loss of around 0.7% at 500 °C, with an additional 0.5% loss seen for the PDA functionalised PMMs further functionalised with MPYR. These data support XPS analyses, evidencing successful functionalisation of the PMMs.

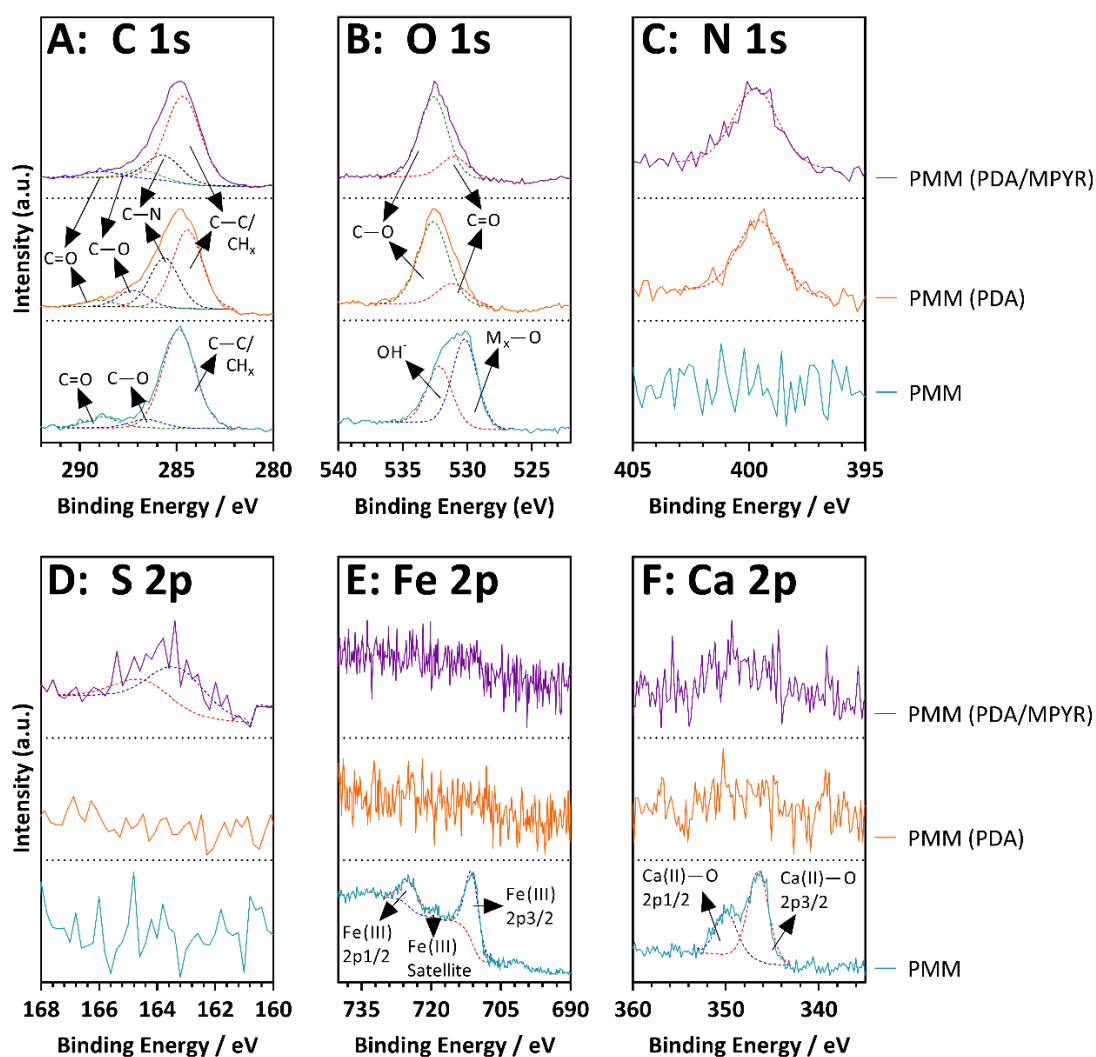


Figure 5. XPS high-resolution spectra of unfunctionalized, PDA and PDA/MPYR functionalised high porosity magnetic microspheres.

3.4 Preparation, structure, and particle attributes of magnetic framework composites (MFCs)

To assess the prospect of using functionalised PMMs to form MFCs, the archetypal MOF HKUST-1 was selected for initial experiments. Further trials were then conducted with a novel carbon-capture MOF, SIFSIX-3-Cu. HKUST-1⁴⁶ is a copper-based MOF containing trimesic acid linkers and has been extensively studied for applications spanning the adsorption and separation of gases, organics and ions; to catalysis, sensing, and composites for wastewater treatment^{73–75}. SIFSIX-3-Cu has been more recently discovered and identified as a promising material for carbon capture and storage due to its high capacity and selectivity for CO₂^{47,76}.

A layer-by-layer method (sequentially moving the functionalised PMMs between two solutions, one containing the MOF linker and another containing the metal salt precursor) was selected to prepare the MFCs due to the high level of control it offers for heterogeneous MOF growth on the PMM surfaces. PDA was selected since it has been reported to attach HKUST-1 owing to functional group binding sites⁶⁵. TGA results confirm successful loading of HKUST-1 on the PDA functionalised PMMs and enabled quantification of MOF loading from the percent weight loss of the sample upon thermal decomposition of the MOF (Figure 6). A HKUST-1 loading of (10 ± 2) wt.%, was calculated using a moisture normalised pure MOF decomposition as 45% between 280 and 400 °C⁷⁷. For the SIFSIX-3-Cu MOF, we first prepared PDA functionalised PMMs, and then employed a novel strategy which involved further reacting the PDA functionalised PMMs with MPYR to affix pyridine functional groups to the PMM surfaces⁶⁵. Pyridine functional groups provide nitrogen coordination sites for SIFSIX-3-Cu (which itself contains pyrazine linkers). Figure 6 'B' shows thermograms for PDA and PDA/MPYR functionalised PMMs and the resulting SIFSIX-3-Cu MFCs. A higher SIFSIX-3-Cu loading can clearly be identified for the PDA/MPYR functionalised PMMs (11 ± 1) wt.% compared to PMMs functionalised solely with PDA (8 ± 1) wt.%, calculated using a moisture normalised pure SIFSIX-3-Cu decomposition as 70.3 wt.% between 125 and 250 °C (measured herein, Figure S5, Supplementary Information). This difference in SIFSIX-3-Cu loading leads us to

conclude that the secondary functionalisation of PDA with MPYR is beneficial in promoting SIFSIX-3-Cu MOF nucleation and growth on the PMM surfaces, likely due to the enhanced interaction between the pyridine functional groups on the PMM surface and Cu(II) in the MOF.

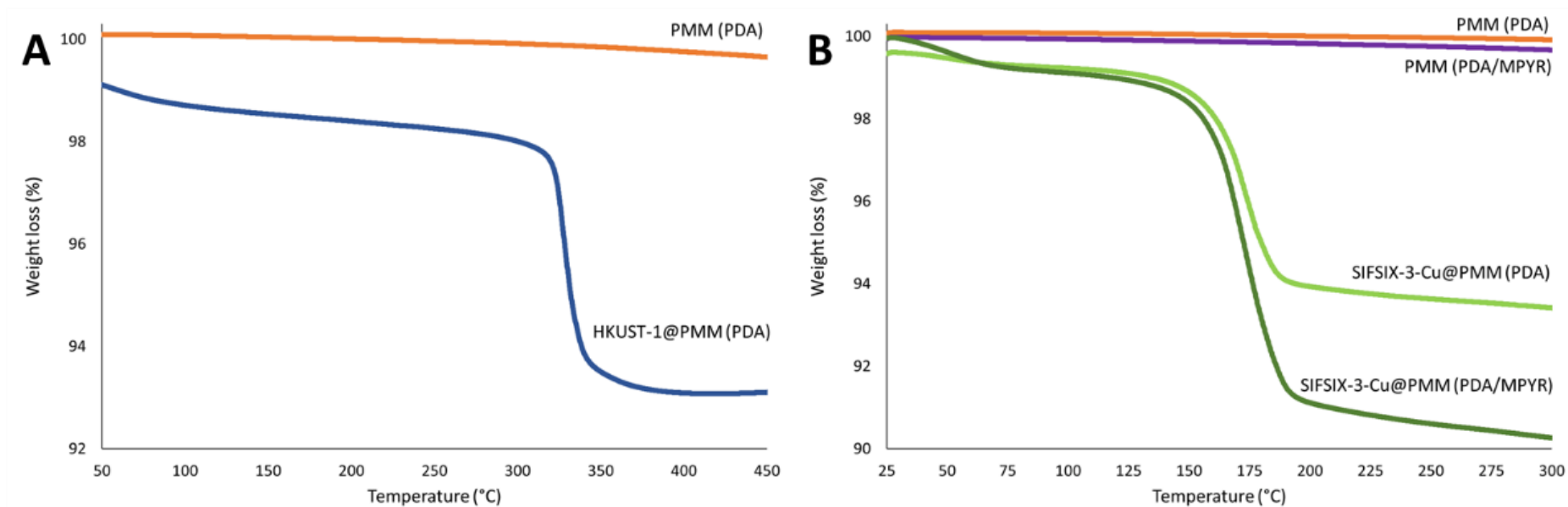


Figure 6. TGA data of: A, PDA functionalised PMMs (orange) and HKUST-1@PMM (PDA) MFC (dark blue); B, PDA (orange) and PDA/MPYR (purple) functionalised PMMs and SIFSIX-3-Cu@PMM (PDA) (light green) SIFSIX-3-Cu@PMM (PDA/MPYR) (dark green) MFCs.

SEM and EDS analyses were used to examine the morphology, surface coverage and placement of MOF crystals on the MFCs with the highest MOF loadings. Images of HKUST-1@PMM (PDA) MFC are displayed in Figure 7. These images show that the PMMs are coated in a discontinuous layer of irregular shaped HKUST-1 nano-crystals, which can also be seen inside some of the microsphere pores. The copper signal in the EDS analysis provides compelling evidence for the presence of HKUST-1 MOF on the surface of the PMMs, giving an approximately 36 wt.% coverage of the MOF. Figure 8 shows SIFSIX-3-Cu@PMM (PDA/MPYR), also showing MOF nano-crystals on the surfaces and in some of the pores of the PMMs. EDS mapping of SIFSIX-3-Cu@PMM (PDA/MPYR) MFC exhibits signals for copper, silicon, and fluoride ions present in SIFSIX-3-Cu. The red circles in Figure 8 highlight an area of high MOF concentration. Using the copper EDS signal, the SIFSIX-3-Cu coverage on the surface of the PDA/MPYR functionalised PMM was determined as approximately 61 wt.%. EDS elemental analyses of HKUST-1@PMM (PDA) and SIFSIX-3-Cu@PMM (PDA/MPYR) MFCs, show that MOFs can be loaded on functionalised PMMs. The substantially higher surface coverage of MOF on SIFSIX-3-Cu@PMM (PDA/MPYR) MFC compared to MOF on the HKUST-1@PMM (PDA) MFC (61% and 36%) with similar total weight loadings (11% and 10%) implies that the SIFSIX-3-Cu is more evenly spread over the functionalised PMM surface compared to HKUST-1. This observation is indicative of more concentrated areas of HKUST-1 where the MOF preferentially builds on itself, as in secondary growth type methods⁷⁸. This result is also supported by the copper EDS signals (green) in Figure 7 and Figure 8, which show more intensely bright areas in HKUST-1@PMM (PDA) MFC compared to SIFSIX-3-Cu@PMM (PDA/MPYR) MFC. These brighter areas in both MFCs show where more MOF has gathered/grown, possibly due to more protected anchoring points in the porous magnetic microsphere, or conceivably owing to initial MOF attachment and subsequent preferential growth.

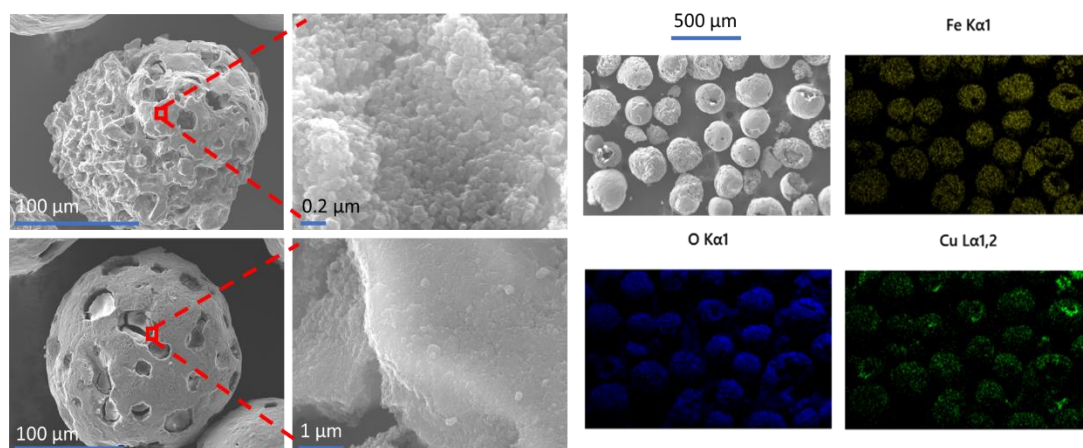


Figure 7. SEM images (left) and EDS elemental mapping (right) of HKUST-1@PMM (PDA) MFC. EDS mapping shows the presence of iron (yellow), oxygen (blue) and copper (green) in the MFC.

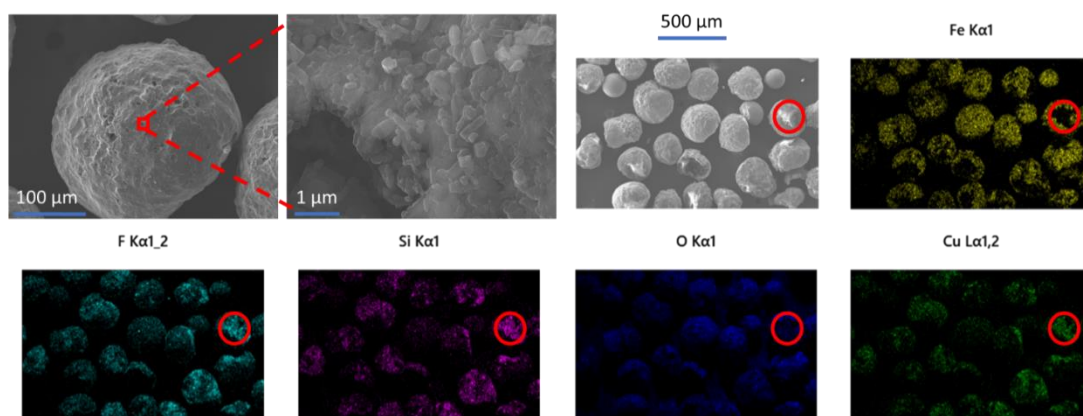


Figure 8. SEM images (top left) and EDS elemental mapping of SIFSIX-3-Cu@PMM (PDA/MPYR) MFC. EDS mapping shows the presence of iron (yellow), fluorine (turquoise), silicon (pink), oxygen (blue) and copper (green) in the MFC. Red circles highlight areas of high SIFSIX-3-Cu MOF concentration.

FTIR and Raman spectroscopic analyses were used to confirm the chemical composition of the MOFs on/in the MFCs. Figure 9 'A' and 'B' show the vibrational spectra of HKUST-1@PMM (PDA) and SIFSIX-3-Cu@PMM (PDA/MPYR). FTIR spectra for both MFCs show the expected absorbances for the MOFs as reported in the literature^{47,79}, including intense diagnostic peaks at 1371 cm^{-1} (assigned as a $\nu_{\text{ip}}(\text{COO})$ vibrational mode of the carboxylate linker in HKUST-1)⁷⁹ and 1435 cm^{-1} (tentatively assigned as a ring bending mode of pyrazine⁴⁷) in the FTIR spectra of HKUST-1@PMM (PDA) and SIFSIX-3-Cu@PMM (PDA/MPYR), respectively. Optical and Raman imaging (inset in Figure 9 'B') confirmed the discontinuous surface coverage of MOFs on the MFCs, with higher, more uniform coverage observed on the SIFSIX-3-Cu@PMM (PDA/MPYR) MFC, relative to HKUST-1@PMM (PDA) MFC, consistent with EDS

mapping. The Raman spectra collected from sky blue areas in the optical images of HKUST-1@PMM (PDA) match that expected for the HKUST-1 MOF⁷⁹. Interestingly, the intensity of the band at 1705 cm⁻¹ (assigned as a $\nu_{\text{ip}}(\text{COOH})$ in benzene-1,3,5-tricarboxylic acid) is more intense in many of the Raman spectra captured from different sky blue domains on the MFCs than that observed in the reported pristine HKUST-1 MOF spectrum. This suggests a high density of structural defects where Cu-Cu moieties are not always included in the framework thus resulting in the transformation of carboxylates to carboxylic acids⁷⁹. However, hydrogen bonding between adjacent couples of COOH groups likely preserve continuity of the MOF network. Spectra obtained from white areas of the SIFSIX-3-Cu@PMM (PDA/MPYR) MFC are consistent with that obtained from the pristine SIFSIX-3-Cu MOF (Figure S6, Supplementary Information) and with the vibrational modes of the pyrazine linker (1044, 1519 and 1627 cm⁻¹) and SiF₆ structural motifs (677 and 705 cm⁻¹), as reported previously in the Raman spectra of structural analogues⁸⁰. It is interesting to note the majority of MOF peaks in FTIR spectra of the MFCs are downshifted relative to those reported in the literature for the respective MOFs. This shift likely indicates that the MOF networks are subject to tensile strain, reflecting the complex surface topography and local curvature of the microsphere upon which the MOF is grown/attached. Raman maps of the MFCs with further analyses are detailed in Figures S7 and S8 in the Supplementary Information.

PXRD was used to examine the crystal structures present in the MFCs. Figure 9 'C' shows the diffractogram of HKUST-1@PMM (PDA) MFC, appearing as an approximate superposition of the patterns of the pristine PMM (experimental) and pristine HKUST-1 MOF (calculated). The sharp peak at 6° 2 θ can be seen in both the MOF and the MFC evidencing crystallinity, though many of the other peaks for HKUST-1 are not observed due to the low MOF concentration present in the MFC. The high relative intensity of the 6° 2 θ peak compared to the other peaks for HKUST-1 at higher °2 θ could result from a highly ordered and preferentially oriented crystalline material, which has been observed elsewhere with HKUST-1 when using the layer-by-layer synthesis method⁸¹. The small crystals produced by the layer-by-layer process and the slow crystal growth from the low synthesis temperature (room

temperature then 50 °C) used herein could also result in some peak broadening, lowering the intensities of the HKUST-1 peaks in the HKUST-1@PMM (PDA) MFC diffraction pattern⁸². This XRD result supports the stronger IR and Raman evidence for the HKUST-1 structure on the PMM surface. Figure 9 'D' shows the diffractogram of SIFSIX-3-Cu@PMM (PDA/MPYR) MFC against the pristine PMM and pristine SIFSIX-3-Cu MOF. Peaks corresponding to both SIFSIX-3-Cu and PMMs can be seen in the PXRD pattern of the MFC, confirming the presence and crystallinity of SIFSIX-3-Cu MOF on the PDA/MPYR functionalised PMMs. The relative intensities of peaks corresponding to SIFSIX-3-Cu (e.g. at 13 and 17° 2 θ) change slightly in the MFC diffraction pattern, possibly owing to hydration of the MOF or slight changes in the crystal structure of the MOF when grown on the surface of the PMMs⁷⁶.

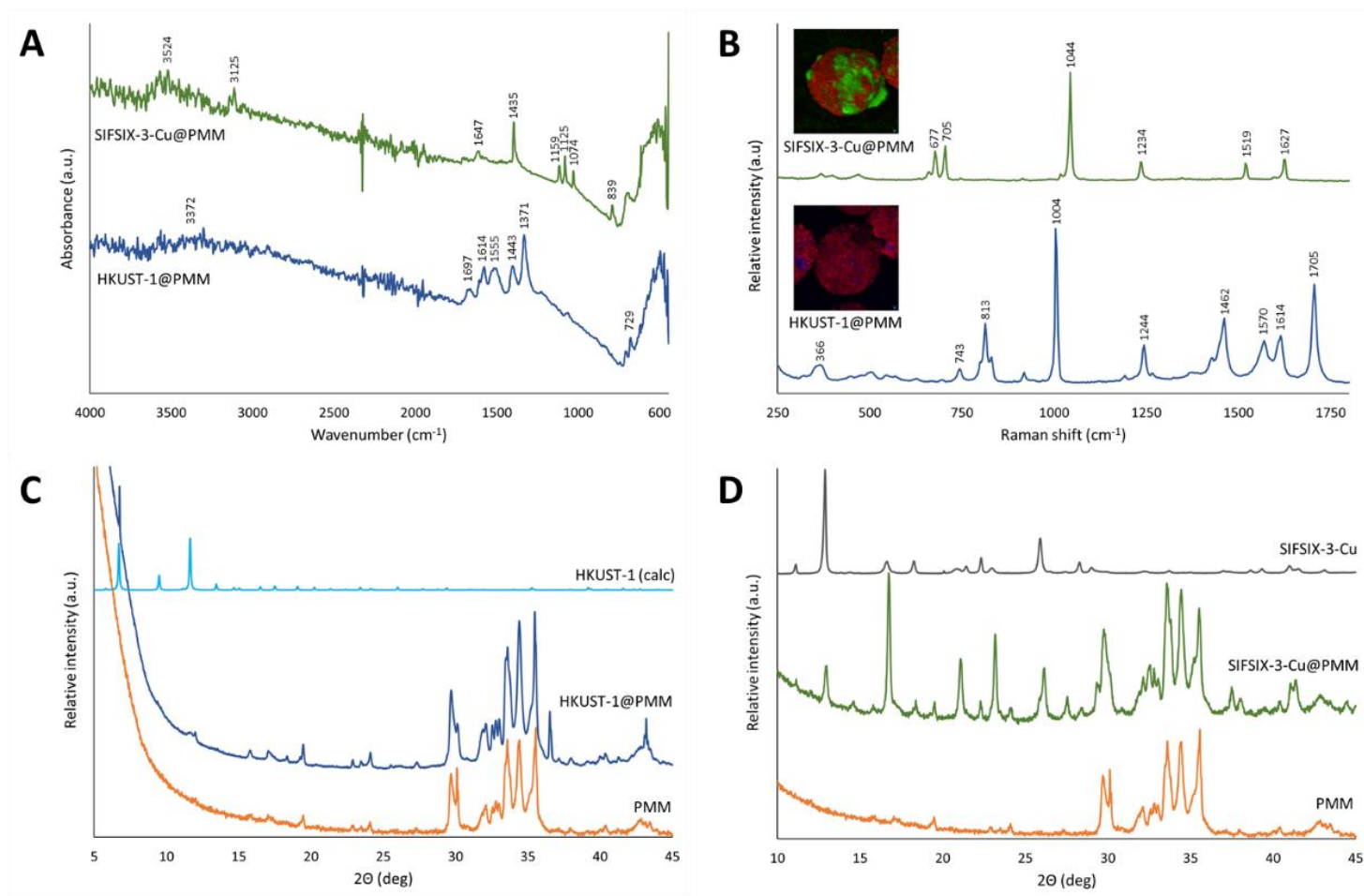


Figure 9. Structural characterisation of SIFSIX-3-Cu@PMM (PDA/MPYR), and HKUST-1@PMM (PDA) MFCs and pristine PMMs. A, FTIR absorbance spectra; B, Confocal Raman microscopy analysis obtained from MOF-rich regions of the respective MFCs, insets are false colour images depicting the distribution of SIFSIX-3-Cu (green, top) or HKUST-1 (blue, bottom) and PDA (red) in representative MFCs (see Supplementary Information for further details), scale bars are 10 microns; C and D, powder X-ray diffraction patterns.

The micro-porosity of the MFCs was evidenced by Kr gas sorption analyses. Mercury intrusion was not used on the MFCs as it cannot measure smaller pore sizes (<6 nm), it requires gram-scale quantities and is destructive. It is assumed that the macro-porosity of the PMMs is retained after MOF growth as the small (nm-scale) MOF crystals are seen to coat the PMM surfaces rather than block the large micron-scale pores (see Figure 7). Kr was used as the gas sorbate (rather than N₂ or CO₂) owing to the thin coating of MOF present in the MFCs⁸³. Figure 10 shows the Kr sorption isotherms and the cumulative pore volume plots for HKUST-1@PMM (PDA) and SIFSIX-3-Cu@PMM (PDA/MPYR) MFCs for pore widths between 1.75 and 20 nm. Data labelled 'Total' represents the MFCs, and data labelled 'PMM subtracted' correspond solely to the respective MOFs for each MFC, determined by subtracting the contribution of Kr sorption for PMMs from the MFCs, and accounting for the mass of MOF present in the MFCs. Both MFCs exhibit micro-porosity owing to the MOF pores, however the total pore volumes for the MOFs in the MFCs are lower than reported for their corresponding pristine MOF powders by N₂/CO₂ adsorption. This is possibly as pore widths less than 1.75 nm could not be mapped using the Kr sorption method as the instrument cannot start at <0.01 P/P₀. Nevertheless, micro-porosity is demonstrated in both samples due to the MOF attachment.

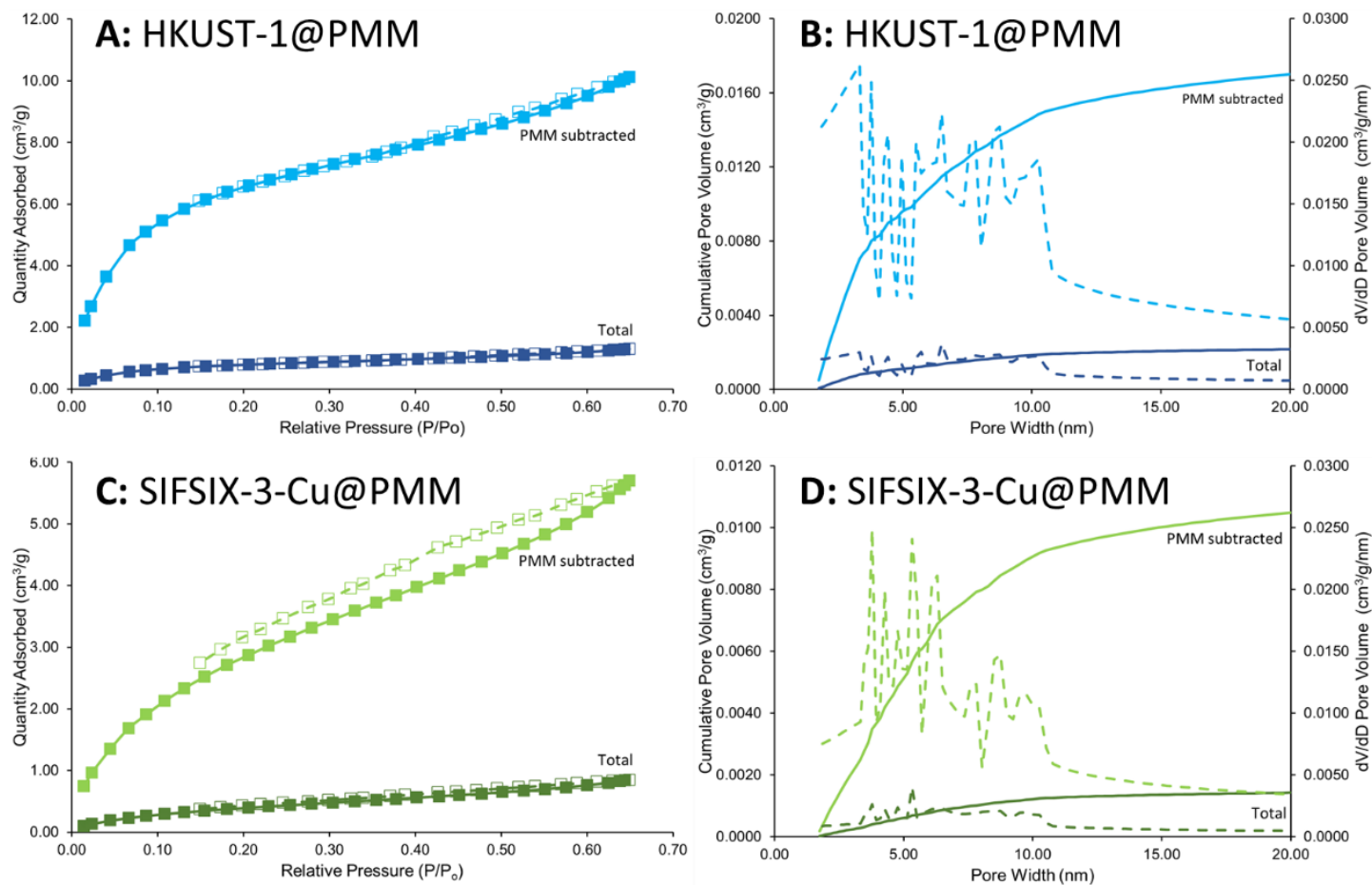


Figure 10. Kr adsorption-desorption isotherms and cumulative pore volume plots for SIFSIX-3-Cu@PMM (PDA/MPYR) (A, B) and (HKUST-1@PMM (PDA) MFCs (C,D). Data labelled 'total' represents the MFCs, and labelled 'PMM subtracted' represents the respective MOFs for each MFC, determined by subtracting the contribution of Kr sorption for PMMs from the MFCs, and accounting for the mass of MOF present in the MFCs. Data collected at -196 °C. Pore volume/size distribution (1.75-20 nm) was acquired from an extension of the BJH model by Chao et al⁵⁰.

Overall, we have demonstrated a new route to producing MFCs with PMMs and MOFs HKUST-1 and SIFSIX-3-Cu, showing attachment and growth of the MOFs on the PMM surfaces. These demonstrate macro-micro hierarchical porosity from the iron/calcium oxide microsphere and MOF components respectively, and contain strong magnetic properties which could benefit many applications, as previously highlighted.

4 Conclusions

In this study a novel rapid, scalable and solvent-free flame-spheroidisation process was optimised for the sustainable production of both high porosity (iron/calcium oxides) and low porosity (magnetite) magnetic microspheres in the size range of 50 to 300 μm . The high porosity microspheres exhibited strong magnetisation (M_s : 25 emu/g) alongside a very high intraparticle porosity of 95% (pore diameter: $12.4 \pm 13.4 \mu\text{m}$). The low porosity microspheres demonstrated extremely high magnetisation (M_s : 91 emu/g) with an intraparticle porosity of 52%. Both materials showed ferrimagnetic behaviour with low remnant magnetisations. The crystalline and mineral compositions of the magnetic microspheres were elucidated through detailed XRD and MLA studies, followed by an investigation into their rapid induction heating capabilities, with both the high and low porosity microspheres showing an $\approx 80^\circ\text{C}$ rise over 30 s at only 120 W. These products represent a substantial advancement in the field of magnetic microspheres due to their simple and cost-effective manufacture and the high porosities and room-temperature magnetisations that can be obtained. The microspheres would be suitable to a range of applications, benefiting from ease of detection, magnetic field separation and efficient induction heating.

An in-depth XPS analysis revealed the successful surface functionalisation of the PMMs with 0.7-1.2 wt.% PDA and MPYR. A controlled layer-by-layer heterogeneous MOF growth strategy was used on the functionalised PMMs to form innovative

magnetic framework composites with archetypal MOF HKUST-1 (10 wt.% loading, 36 wt.% surface coverage) and the advanced carbon-capture MOF SIFSIX-3-Cu (11 wt.% loading, 61 wt.% surface coverage). The tailored technique of further functionalising the PDA surface with MPYR was found to improve MOF loading for SIFSIX-3-Cu from 8 to 11 wt.%. EDS and Raman mapping revealed the distribution of the MOFs on the PMM surfaces, while FTIR and XRD confirmed the MOF chemical compositions and crystallinities. These materials are the first example of MFCs using a single-material porous magnetic scaffold, in addition demonstrating macro-micro hierarchical porosity (pores $>1\ \mu\text{m}$ and $<10\ \text{nm}$) by Kr adsorption and mercury intrusion porosimetry. The MFCs have potential to be used in various applications from catalysis to the adsorption and separation of gases, organics and ions for environmental remediation. Our adaptable synthetic approach is applicable to a variety of different MOFs, opening the possibility of diverse properties and consequent applications.

5 Author contributions

John Luke Woodliffe: Conceptualization, Formal Analysis, Validation, Funding Acquisition (via Henry Royce Institute), Investigation, Methodology, Writing – Original Draft, Writing – Review & Editing, Visualization. Jesús Molinar-Díaz: Funding Acquisition (via Henry Royce Institute), Investigation, Writing – Review & Editing, Visualization. Md Towhidul Islam: Methodology, Writing – Review & Editing. Lee A. Stevens: Investigation, Methodology, Validation, Writing – Review & Editing, Visualization. Matthew D. Wadge: Formal Analysis, Investigation, Writing – Original Draft, Writing – Review & Editing, Visualization. Graham A. Rance: Investigation, Validation, Writing – Original Draft, Writing – Review & Editing, Visualization. Rebecca Ferrari: Conceptualization, Supervision, Writing – Review & Editing. Ifty Ahmed: Conceptualization, Supervision, Writing – Review & Editing. Andrea Laybourn: Conceptualization, Project Administration, Supervision, Writing – Review & Editing, Funding Acquisition (EPSRC CDT).

6 Conflicts of interest

The authors declare no competing financial interest.

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Supporting Information

Rapid synthesis of magnetic microspheres and the development of new macro-micro hierarchically porous magnetic framework composites

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Porous Magnetic Microspheres

SEM micrographs of varying mixing/grinding types

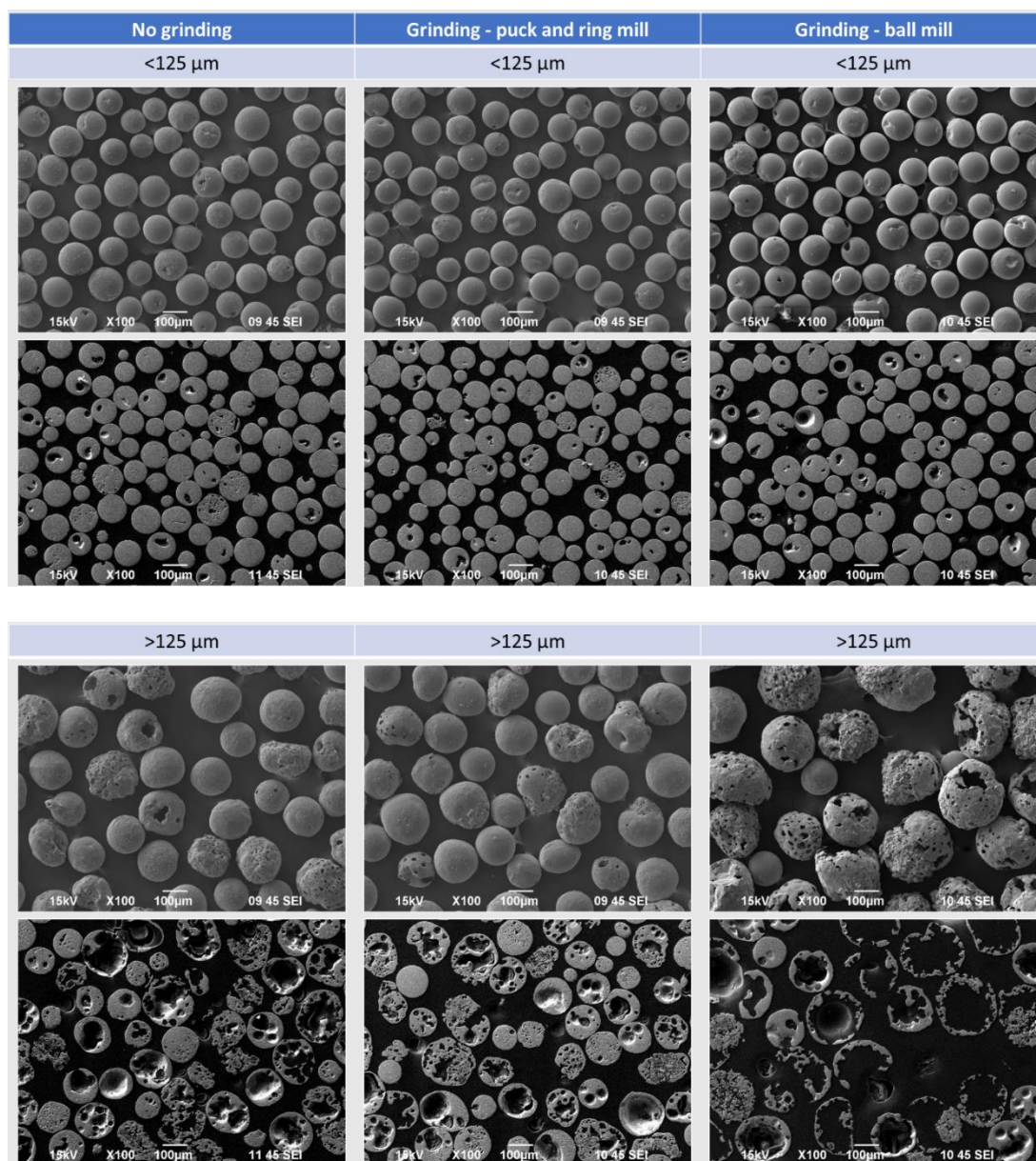


Figure S1. SEM micrographs of powders and cross sections of resultant porous magnetic microspheres produced without grinding and with grinding (of Fe_3O_4 with CaCO_3) using a puck and ring or ball mill. $>125\ \mu\text{m}$ and $<125\ \mu\text{m}$ fractions have been separated. Mixing in a ball mill led to increased porosity compared with simple mixing without grinding (pestle and mortar) or grinding with a puck and ring mill.

Pore size distribution of high porosity microspheres

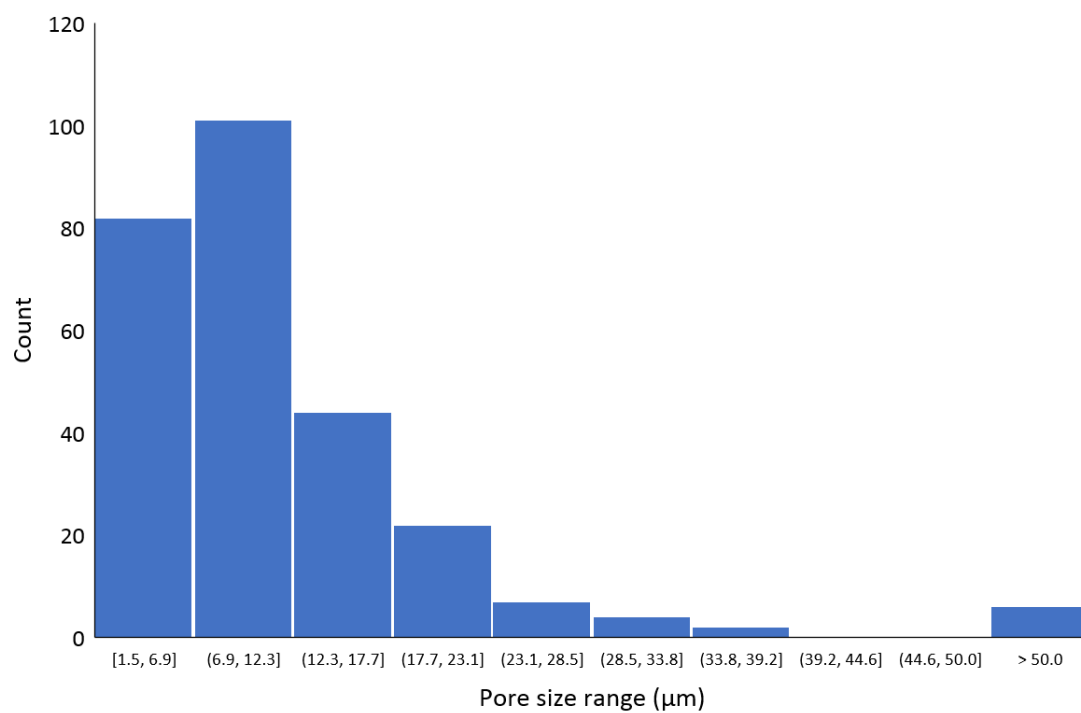


Figure S2. Histogram showing the size distribution of the pores in the porous microspheres by SEM image analysis.

Surface Functionalised Microspheres

TGA analysis

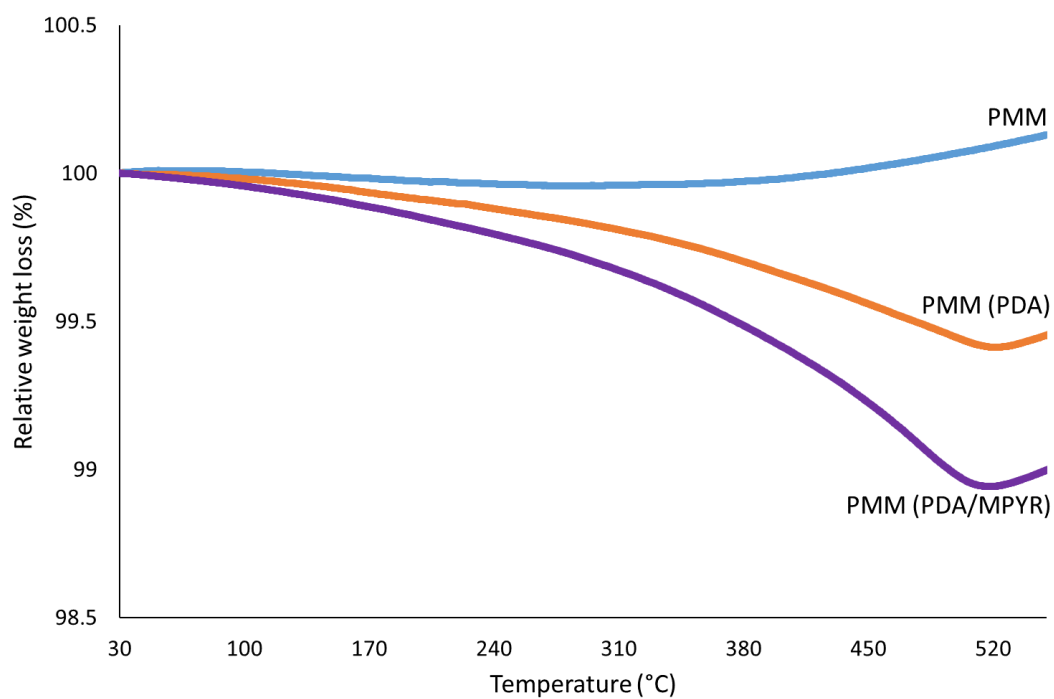


Figure S3. Thermal decompositions of unfunctionalised PMMs, and PMMs functionalised with PDA and PDA/MPYR.

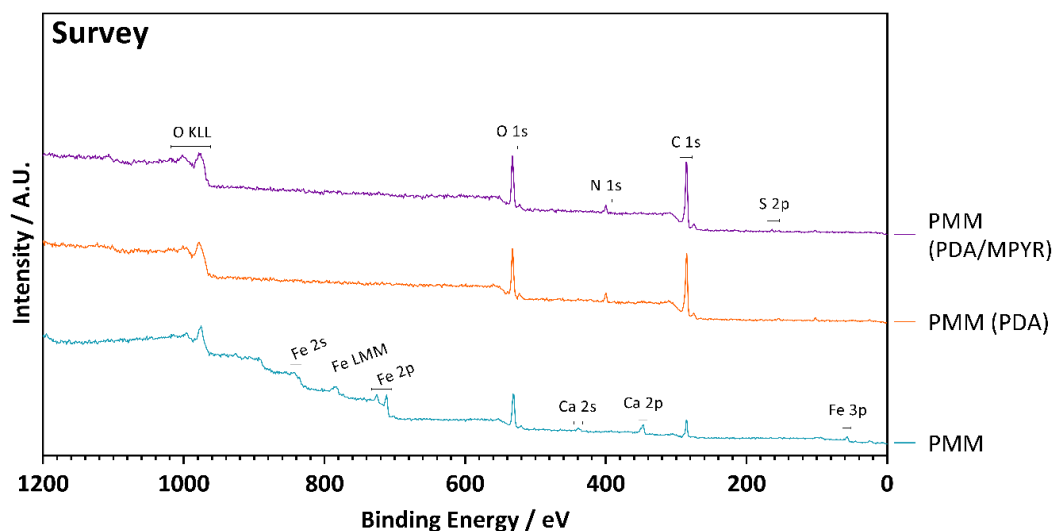


Figure S4. Survey XPS spectra of unfunctionalised PMMs, and PMMs functionalised with PDA and PDA/MPYR.

A description of the full XPS deconvolutions, including relative atomic quantities, are presented below, and are summarised in Tables S1 and S2.

PMM

The O 1s high-resolution region was fitted to 2 peaks located at 530.2 (60.6%) and 532.2 (39.4%) eV corresponding to metallic oxides and water, respectively. C 1s spectrum was fitted to 3 peaks located at 284.8 (83.5%), 286.6 (7.3%) and 288.9 (9.3%) eV corresponding to adventitious carbon, C—O and C=O, respectively; the latter two being contamination arising from adventitious carbon interaction with oxygen and carbonates, respectively. Both Fe 2p and Ca 2p detailed doublet (j-j coupling) splits. Fe was found to be in its 3+ valence state due to the peak location of 710.8 eV ($\Delta_{\text{ev}} = 13.5$ eV) correlating with magnetite, with the presence of an additional peak between the two spin states, likely to be a Fe 2p satellite peak (718.9 eV). Ca 2p demonstrated a single doublet split (3.5 eV shift), with peak location

(346.5 eV) corresponding to CaO. The Fe peaks could be deconvoluted further to reveal the presence of Fe^{2+} , which is also expected to be present in some of the iron oxides.

PMM (PDA)

PDA layers are anticipated to be very thin (10s of nm^{1,2}), and hence the presence of N 1s and specific C peak fitted in XPS demonstrate a minimum bound on its thickness (5-10 nm). O 1s again was fitted to 2 peaks; however, their locations at 531.2 (ca. 21%) and 532.6 (ca. 79%) eV corresponded to C=O and C—O, respectively, compared to the native microspheres. The binding energy at 532.6 eV is assigned to the oxygen from catechol and quinone form of dopamine³. N 1s was fitted to a single peak located at 399.5 eV, corresponding to PDA species^{4,5}. C 1s, was fitted to 4 peaks; one more than the unfunctionalised microspheres. The peaks presented were located at 284.4 (51.4%), 285.6 (33.6%), 287.2 (10.7%) and 288.9 (4.3%) eV, corresponding to C—C/CH_x, C—N, C—O, and C=O, respectively^{3,6}.

PMM (PDA/MPYR)

Similar to the PDA microspheres, the O 1s spectral features were fairly consistent, except a subtle shift of 0.2 eV for the O=C peak fit. No variations were seen in N 1s peak, however, the C 1s did present subtle peak shifts and relative percentage differences, likely attributed to the different chemical makeup of the surface due to MPYR deposition. 4 peak fittings, which have shifted to 284.7, 285.7, 286.9, and 288.8 eV, with relative percentages of 68.6, 19.9, 6.8, and 4.8 %, respectively, were observed. Most importantly for MPYR identification, the S 2p region detailed a very low intensity doublet peak located at 163.3 eV, which due to the variations in literature values, could either be correlated to unbonded thiol⁷, which may be surface

dominant, rather than overall lack of S bonding to PDA moieties, or could be attributed to S—C bonding⁸.

Table S1. Atomic percentages of different elements in the microsphere samples obtained from fitting of XPS data.

Sample ID	Element (at.% ± S.E.M)					
	O	N	C	S	Fe	Ca
PMM	38.9 ± 1.0	-	47.9 ± 1.1	-	6.1 ± 0.6	7.0 ± 0.5
PMM (PDA)	20.4 ± 0.7	5.9 ± 0.7	73.7 ± 0.9	-	-	-
PMM (PDA/MPYR)	19.7 ± 0.6	4.8 ± 0.6	74.5 ± 0.8	1.0 ± 0.2	-	-

Table S2. Breakdown of XPS peaks in the microsphere samples, with their associated binding energies, corresponding bonds and literature references.

Sample Code	Elements	Binding Energy / eV	Corresponding Bonds (Area / %)	Refs.
PMM	O 1s	530.2	M _x —O (60.6)	9
		532.2	O—H (39.4)	
	C 1s	284.8	C—C/CH _x (83.5)	10
		286.6	C—O (7.3)	
		288.9	C=O (9.3)	
	Fe 2p	711.1 (2p 3/2) Shift $\Delta_{\text{eV}} =$ 13.5 eV	Fe(III)—O	9,11,12
	Ca 2p	346.5 (2p 3/2) Shift $\Delta_{\text{eV}} =$ 3.5 eV	Ca(II)—O	13
PMM (PDA)	O 1s	531.2	O=C (21.3)	4
		532.6	O—C (78.7)	
	N 1s	399.7	N—H (100)	4,5
	C 1s	284.4 285.6 287.2 288.9	C—C/CH _x (51.4) C—N (33.6) C—O (10.7) C=O (4.3)	3,6
PMM (PDA/MPYR)	O 1s	531.0	C=O (21.5)	3,4
		532.6	C—O (78.5)	
	N 1s	399.5	N—H (100)	4,5

	C 1s	284.7 285.7 286.9 288.8	C—C/CH _x (68.6) C—N (19.9) C—O (6.8) C=O (4.8)	3,6
	S 2p	163.3 (2p 3/2) Shift $\Delta_{\text{eV}} = 1.2$ eV	S—H or S—C	7,8,14

Magnetic Framework Composites

Synthesis of pristine MOF SIFSIX-3-Cu

Based on previously published method¹⁵, a 5 mL pyrazine in methanol solution (0.300 g, 3.75 mmol) was layered onto a 5 mL CuSiF₆·H₂O in methanol solution (0.325 g, 1.45 mmol) and left at room temperature for 24 hours in a glass vial. The product was collected by centrifuge and washed with methanol (40 mL x 3) before drying in an oven at 50 °C for 2 hours.

TGA of pristine MOF SIFSIX-3-Cu

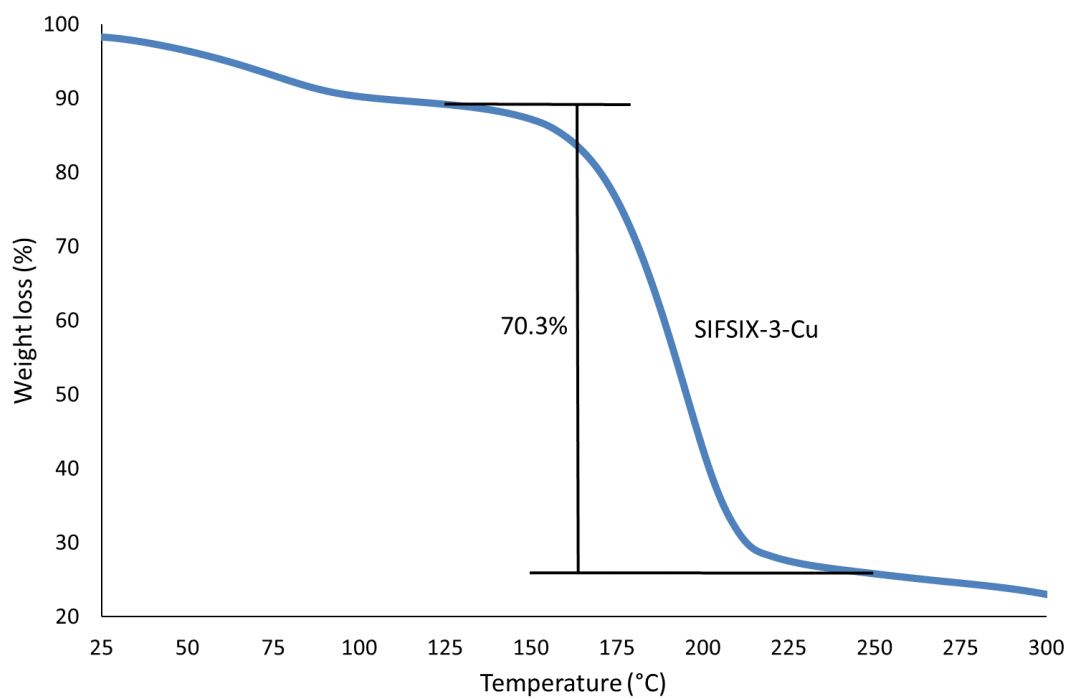


Figure S5. Thermal decomposition of MOF SIFSIX-3-Cu under N₂ gas at a 10 °C/min ramp rate. Main decomposition between 125 and 250 °C characterised as a 70.3% weight loss when normalised for moisture content.

Raman analysis of pristine MOF SIFSIX-3-Cu

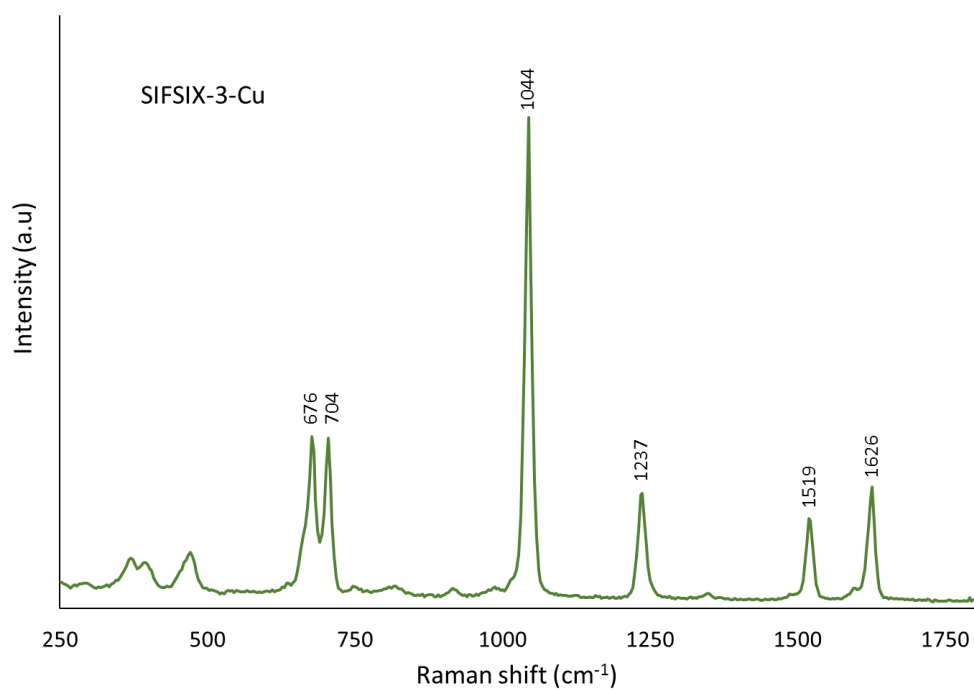


Figure S6. Raman spectrum of pristine MOF SIFSIX-3-Cu.

Raman mapping of MFCs

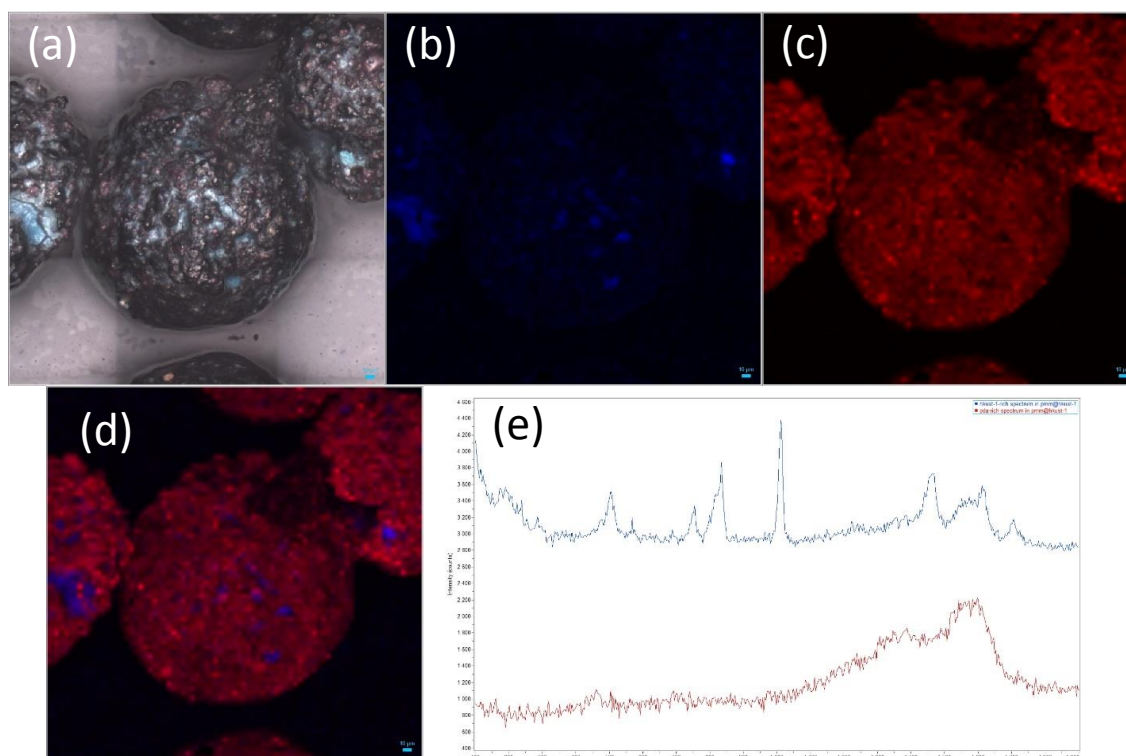


Figure S7. Confocal Raman microscopy analysis of HKUST-1@PMM (PDA). Blue scale bar in bottom right is 10 μm . (a) Optical micrograph and (b-d) Raman maps of a typical HKUST-1-coated PMM. The blue map (b) shows the intensity of the band within the range 960-1060 cm^{-1} (* centred at 1011 cm^{-1}) diagnostic of HKUST-1 (assigned as an in-plane bending mode of the aromatic ring of the benzene-1,3,5-tricarboxylate linker, $\delta(\text{C-C-C})_{\text{R}}$)¹⁶. It is important to note that areas of blue colouration in (b) closely match areas of sky blue colouration in the optical image (a). The red map (c) shows the intensity of the bands within the range 1100-1800 cm^{-1} (***) diagnostic of PDA¹⁷. In (d) the blue and red maps are overlaid, with the intensities normalised for visual impact. Scale bars in (a-d) are 10 microns. (e) Representative point spectra from HKUST-1-rich (top, blue trace) and PDA-rich (bottom, red trace) areas of the assessed microsphere. Spectra have been offset on the y-axis for ease of comparison.

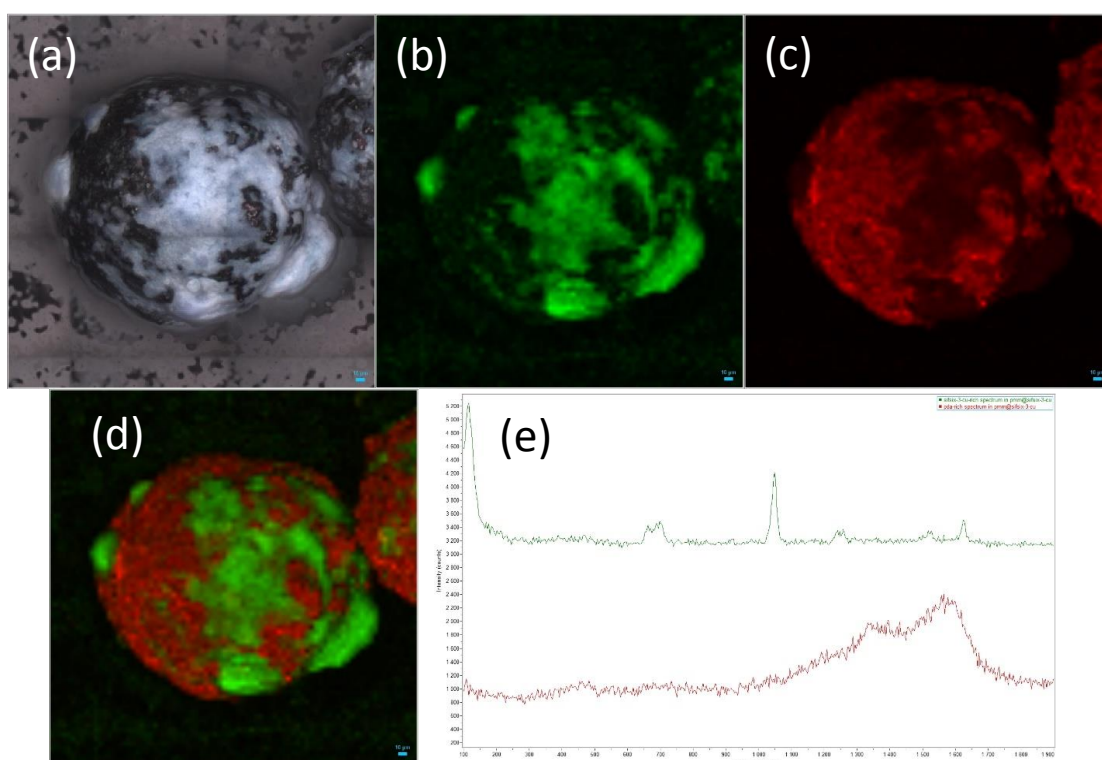


Figure S8. Confocal Raman microscopy analysis of SIFSIX-3-Cu@PMM (PDA/MPYR). Blue scale bar in bottom right is 10 μm . (a) Optical micrograph and (b-d) Raman maps of a typical SIFSIX-3-Cu-coated PMM. The green map (b) shows the intensity of the band within the range 990-1100 cm^{-1} (*, centred at 1046 cm^{-1}) diagnostic of SIFSIX-3-Cu (tentatively assigned as a ring bending mode of the pyrazine linker, based on prior reports of structural analogues)¹⁸. It is important to note that areas of green colouration in (b) closely match areas of white colouration in the optical image (a). The red map (c) shows the intensity of the bands within the range 1100-1800 cm^{-1} (**) diagnostic of PDA¹⁷. In (d) the green and red maps are overlaid, with the intensities normalised for visual impact. Scale bars in (a-d) are 10 microns. (e) Representative point spectra from SIFSIX-3-Cu-rich (top, green trace) and PDA-rich (bottom, red trace) areas of the assessed microsphere. Spectra have been offset on the y-axis for ease of comparison.

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Appendix 3

Rapid microwave synthesis of sustainable magnetic framework composites of UTSA-16(Zn) with Fe₃O₄ nanoparticles for efficient CO₂ capture

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Statement of contribution

- Woodliffe J. L.: literature review/research, laboratory experiments, analysis and characterisation, creation of figures/graphs/tables, writing original draft, review & editing, topic & idea (MFCs using UTSA-16(Zn) and Fe₃O₄ nanoparticles in microwave synthesis) conceptualisation
- Johnston A.: contribution to MNP-CA synthesis methodology and experimental write-up, review & editing
- Fay M.: analysis (TEM)
- Ferrari B.: review & editing, topic conceptualisation
- Gomes R. L.: review & editing
- Lester E.: review & editing
- Ahmed I.: review & editing, topic conceptualisation
- Laybourn A.: review & editing, topic conceptualisation

Rapid microwave synthesis of sustainable magnetic framework composites of UTSA-16(Zn) with Fe₃O₄ nanoparticles for efficient CO₂ capture

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Abstract

Metal-organic frameworks (MOFs) have shown excellent potential for carbon dioxide capture applications due to their high sorption capacities and selectivities. However, MOFs are typically thermally insulating, and so thermal CO₂ regeneration is challenging, especially on the large scales required in industry. This limitation can be overcome by inclusion of magnetic nanoparticles within the MOF structure, enabling rapid and energy efficient CO₂ regeneration using induction heating. To this end we have developed novel magnetic framework composites (MFCs) comprised of MOF UTSA-16(Zn) (UTSA: University of Texas at San Antonio, a Zn-based MOF with citrate linkers) and Fe₃O₄ nanoparticles. Our work also addresses the sustainability and scalability challenges faced by MFCs required for industrial application, considering the use of only inexpensive and widely-available materials.

Herein we report a two-step procedure for preparing the MFCs. Firstly, a scalable single-step continuous hydrothermal synthesis method is used to produce highly pure, stable, and crystalline citrate-coated Fe₃O₄ nanoparticles (62% yield). The

nanoparticles exhibit a uniform particle size (19 ± 11 nm) and a very high saturation magnetisation (78 emu/g) compared with previously published citrate-coated Fe_3O_4 nanoparticles. Next, various concentrations (2.6-18.7 wt.%) of these nanoparticles were incorporated into UTSA-16(Zn) via a rapid microwave-assisted direct-growth strategy (10 min) to form the MFCs (81-83% yield). The MFCs demonstrate high CO_2 adsorption capacities (2.8-3.3 mmol/g) and recyclability. In addition, the MFCs heat rapidly in an applied magnetic field for CO_2 release, reaching regeneration temperatures in remarkably short times (e.g. 60 °C in 8 seconds).

The MFCs developed in this work thus combine strong CO_2 adsorption profiles and substantial regeneration heating capabilities, while being produced in a scalable and sustainable manner. Methods used to prepare MFCs herein are also applicable to other MOFs, opening routes to a variety of sustainable MFCs for impact across a range of applications across carbon capture and triggered release of other guest molecules.

1 Introduction

Since the industrial revolution, a sharp increase in atmospheric concentrations of the greenhouse gas carbon dioxide (CO₂) has been observed from 180-280 ppm to over 400 ppm¹⁻³. This increase has significant negative implications for the environment and society⁴, likely resulting in 250,000 additional deaths worldwide annually between 2030 and 2050⁵. Governments around the world are setting net zero CO₂ emissions targets by 2050-2070 in line with the recent report from the Intergovernmental Panel on Climate Change (IPCC)⁶, and have affirmed their commitments in Glasgow 2021 at COP26⁷. Addressing these IPCC targets requires immediate action, preventing CO₂ from entering the atmosphere.

The largest contributor to global anthropogenic CO₂ emissions are coal-fired power plants (10.1 Gt in 2018, 30% of total emissions)^{8,9}. Post-combustion CO₂ capture facilities can be retrofitted into these existing power stations to capture the CO₂ at source¹⁰. However, the current aqueous amine absorption technologies for this process have high energy requirements for separation and purification, increasing a power plant's energy demand by 25-40%¹¹. Alternatives have been investigated such as physical sorbents, membranes, chemical looping and solid sorbents (e.g. porous carbons, zeolites, alumina and metal-organic frameworks (MOFs)¹¹). Of these alternatives, solid sorbents possess many advantages for industrial-scale carbon capture. One major advantage is a reduced energy for CO₂ regeneration, as the CO₂ is physically adsorbed to the material surface, rather than bound by chemical bonds which would need to be broken to release the CO₂¹². Other advantages include a greater uptake capacity and selectivity for CO₂¹².

Metal-organic frameworks are porous materials containing metal ions/clusters and organic linkers.¹³ MOFs are of particular interest to researchers due to their tuneable natures, high porosities and internal surface areas¹⁴. These properties result in the potential for excellent CO₂ adsorption profiles, optimisable for specific flue gas conditions¹⁵. The next phase of development for carbon capture MOFs is consideration of sustainability, scalability, and industrial process design¹⁵⁻¹⁷. This stage requires cost-effective materials with high thermal and chemical stabilities and

the development of energy-efficient processes. During the carbon capture process, MOFs can undergo a temperature swing adsorption procedure¹⁸. Once saturated with CO₂, the MOFs are heated to release the CO₂ after each capture cycle. This regenerates the material for re-use in the next cycle. However, the thermally insulating nature of MOFs make thermal regeneration challenging, especially at scale¹⁹. A newly emerging approach is to incorporate magnetic nanoparticles (MNPs) in MOFs forming magnetic framework composites (MFCs), enabling rapid and highly energy-efficient regeneration of the composites by localised magnetic induction heating²⁰. This process, coined magnetic induction swing adsorption (MISA)²¹, requires remarkably low carbon capture energy costs (1.29 MJ/kgCO₂²², *cf.* 3-4 MJ/kgCO₂ for amine solvents²³). MFCs have also found application across adsorption, sensing, biomedicine, catalysis, and environmental monitoring and water remediation among others^{24–31}.

Aside from their use in MFCs, MNPs are an important class of nanomaterials which have been widely studied. The unique properties of their magnetism, size and surface area/volume ratio have led to applications across biomedicine^{32,33}, nanomedicine³⁴ and sensing³⁵. Surface functionalisation/coating of MNPs is hugely beneficial for their thermodynamic and colloidal stability³⁶. Citrate coatings have been extensively used in the preparation of aqueous-stable MNPs due to the electrostatic, biocompatible, and anti-oxidising properties of citrates, alongside their low cost^{37,38}. Citrates also have chelating properties which can control the crystallite growth of the MNPs and allow them to conjugate to other molecules such as biomolecules and drugs, through the surface carboxyl groups^{37,38}. In this work, a further reason for choosing a citrate coating was the hypothesis that surface citrate groups on the MNPs would promote a binding interaction between the chosen MOF (which contains citrate linkers) and the MNPs.

To be viable for widespread industrial adoption, MFCs (including both the MOF and MNP components) must be produced *via* sustainable and economical routes, with minimal impact on the environment. Typically, the synthesis of MNPs require harsh batch conditions such as high temperatures or reflux for >8 h, often under air sensitive environments such as N₂^{22,39–41}. Subsequent production of MFCs often

requires lengthy MNP surface-functionalisation reactions (e.g. 24 h) required for MOF attachment. This is typically followed by prolonged high temperature autoclave MOF syntheses (e.g. 125 °C for 15 h under Ar) with toxic solvents such as DMF^{22,39,42–44}. The main alternative to autoclave routes is the labour intensive layer-by-layer MOF growth method^{39,40,45}, with a difficult outlook for scale-up due to the amount of time taken and number of steps required to grow the thin MOF layers. The use of expensive MOF linker components and moisture sensitive MOFs is also ubiquitous in MFCs^{22,39,40,42,43,45}. The development of manufacturing processes that reduce product cost and environmental burden of MNPs and MFCs is critical for successful transfer of these materials from the laboratory to industry.

In this paper, we first report a continuous-flow hydrothermal method for producing highly magnetic citrate-coated Fe₃O₄ nanoparticles (MNP-CA) (mean diameter: 19 nm, saturation magnetisation: 78.3 emu/g) via a single step process, with high colloidal stability (Zeta potential: -47.3 mV), purity and crystallinity. This method overcomes the previously mentioned issues of batch reactors, air sensitive environments and lengthy surface-functionalisation steps. We then report a rapid (10 min) microwave-assisted direct-growth strategy to encapsulate various quantities of MNP-CA (2.6-18.7 wt%) in UTSA-16(Zn) (C₁₂H₈KO₁₄Zn₃), a zinc and citrate based MOF chosen for its high CO₂ uptake, good stability to moisture and acid gases and very low reagent costs (<1 USD/g MOF)⁴⁶. The subsequent MFCs are sustainably produced with high yield and CO₂ adsorption capacities (81-83%, 2.8-3.3 mmol/g). The MFCs also show leading processing capabilities for carbon capture, including induction heating up to 150 °C in 30 s and no decrease in adsorption capacity over 12 CO₂ adsorption-desorption cycles. The MNP-CA and the MFC syntheses methods developed herein are transferrable to other MOFs, allowing for the production of a variety of MFCs with wide-reaching impact in alternate applications.

2 Experimental Section

2.1 Materials

All chemicals and reagents were used as received. Zinc acetate dihydrate ($\geq 99.0\%$), citric acid monohydrate ($\geq 99.0\%$), pristine magnetite ($< 5\ \mu\text{m}$, 95%) and potassium hydroxide (86.7%) were obtained from Sigma Aldrich. Ammonium iron(III) citrate (14.5-16% Fe basis) was bought from Honeywell. Methanol ($\geq 99.9\%$) was purchased from Fisher Scientific. Ethanol (absolute, SpS grade) was purchased from Scientific Laboratory Supplies LTD. All water used was deionised.

2.2 Synthesis of citrate-coated Fe_3O_4 nanoparticles

Magnetic magnetite nanoparticles with a citrate coating (MNP-CA) were synthesised using a counter-current continuous hydrothermal reactor set-up (Figure 1), first reported by Lester *et al*⁴⁷. The reactor set-up has been described in more detail for the synthesis of other materials, including barium strontium titanate⁴⁸ and layered double hydroxides⁴⁹. Briefly, aqueous ammonium ferric citrate (0.05 M) was fed unheated via the upflow pump into the reactor at a pre-determined flow rate (10 mL/min). Separately, deionised water was heated to 435 °C in a 2 kW band heater and fed *via* the downflow pump into the top of the reactor at a pre-determined flow rate (20 mL/min). The pressure was maintained in the system at a maximum of 24 MPa by a back-pressure regulator (Swagelok®). The reaction stream was then cooled through a counter-current water heat exchanger and the product in suspension collected at the outlet. Finally, the MNP-CA was allowed to settle, separated by gravity and magnetic attraction, washed with deionised water (3 x 25 mL) then stored in deionised water as a 5 w/v% suspension (yield: 62%).

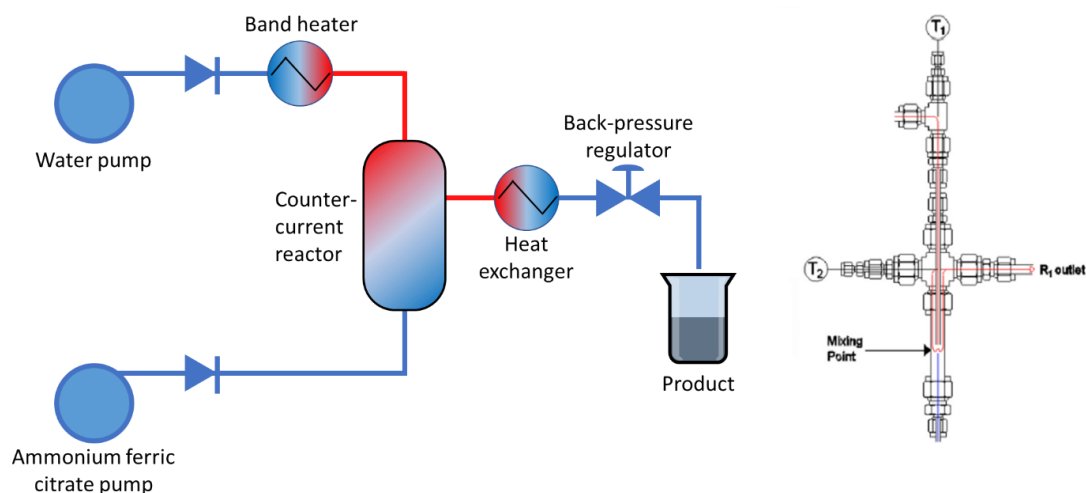


Figure 1: Left: schematic of the counter-current flow reactor set-up for the synthesis of MNP-CA. Right: schematic of the counter-current reactor. T1 and T2: thermocouples in the system.

2.3 Synthesis of MFCs UTSA-16(Zn)@MNP-CA

The synthesis conditions for UTSA-16(Zn) were optimised to inform the conditions for the MFCs. Pristine UTSA-16(Zn) was also used as a comparison to the MFCs (Figure S3, Supplementary Information). The reagents, $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ (0.878 g, 4.0 mmol), citric acid monohydrate (0.840 g, 4.0 mmol) and KOH (0.67 g, 10.4 mmol) were dissolved in H_2O (6–10 mL) in a 35 mL microwave vial. A MNP-CA in H_2O (5 w/v%) solution was added (0–4 mL), bringing the total H_2O quantity to 10 mL. EtOH (10 mL) was added and stirred (10 min) before the vial was sealed and irradiated under autogenous pressure with stirring at a maximum forward power of 300 W (commercial CEM discover microwave reactor, dynamic mode, $T = 60^\circ\text{C}$, $t = 10$ min). After the reaction, the vial was cooled in the microwave cavity with air to $<50^\circ\text{C}$, then the product was collected by washing out the vial with $\text{H}_2\text{O}:\text{EtOH}$ 1:1 (20 mL) followed by centrifugation. The product was then washed and centrifuged with MeOH (3 x 30 mL, 20 mins) before drying in an oven (50°C , >4 h).

2.4 Characterisation

Powder X-ray diffraction (PXRD). X-ray diffraction patterns of the MNP-CA, pristine UTSA-16, and MFCs were obtained using a Bruker D8 Advance DaVinci in Bragg-Brentano geometry, equipped with a Lynxeye 1D detector and motorised air scatter screen. A $\text{Cu K}\alpha$ radiation source was used ($\lambda = 0.15418$ nm) at 40 kV and 40 mA. Scans were conducted between 5° and 65° 2θ , with analysis and pattern matching

performed using Bruker DIFFRAC.EVA software and powder diffraction files from the database⁵⁰.

Scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS). High-resolution SEM images and EDS elemental analyses of the MFCs were taken on a Jeol 7000F FEG-SEM, with an acceleration voltage of 10-15 kV. Secondary electron images were taken at a working distance of 10-11.5 mm with an approximately 10 nm carbon coating, using Jeol PC-SEM software.

Transmission electron microscopy (TEM). TEM was carried out on a JEOL 2100Plus, operating at 200kV and equipped with JEOL STEM detectors. TEM-EDX analysis was run using an Oxford Instruments XMax TLE and Aztec software. Imaging was initially carried out using a Gatan Ultrascan 1000XP CCD camera and Gatan Microscopy Suite 3.21, and then subsequently with a Gatan OneView CMOS detector and Gatan GMS 3.4. To prepare the samples, a 3 μ L drop of the sample suspended in water or ethanol was deposited onto holey carbon grids (Agar Scientific), the excess wicked off after 30 seconds and the grid allowed to dry. MNP-CA size distributions were calculated using Fiji ImageJ software⁵¹.

Infra-red spectroscopy (FT-IR). FT-IR spectra were recorded on a Bruker IFS66 with a KBr beamsplitter. A Globar light source was used with a DTGS room temperature detector and Specac "Goldengate Bridge" diamond ATR attachment. The instrument was air purged using a Parker Balston 75-52 FT-IR Purge Gas Generator.

Thermogravimetric analysis (TGA). TGA was carried out using a TGA550 Discovery (TA Instruments) with an automated vertical overhead thermobalance. Decomposition runs were at a heating rate of 10 °C/min under an air or N₂ atmosphere. CO₂ adsorption runs used the following program: heat to 150 °C under N₂, hold 10 min, cool to 25 °C, switch gas to CO₂, hold 10 min.

N₂ adsorption. N₂ adsorption isotherms were measured at 77K using a Micromeritics Tristar II 3020 instrument. The Brunauer-Emmett-Teller (BET) method was used for surface area calculations.

Vibrating-sample magnetometry (VSM). Magnetometry measurements were taken using 10-40 mg of sample on a SQUID MPMS3 (Quantum Design) at the University of Sheffield via the Royce Institute. Measurements were taken at room temperature with a field strength up to 10 kOe.

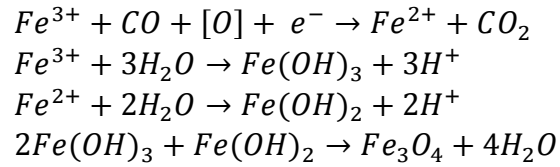
Dynamic light scattering & Zeta potential. Measurements were taken on a Malvern Zetasizer, with samples dispersed in deionised water at 25 °C.

Induction heating. Induction heating measurements were undertaken using a 2 kW induction heater (204 kHz, Cheltenham Induction Heating Ltd.) and the temperature measured with a fibre optic thermocouple (Neoptix Reflex). The thermocouple was placed in a borosilicate glass tube (internal diameter: 11 mm) with 0.67 g of sample powder. The tube was then placed in a water-cooled copper coil (internal diameter: 27 mm, height: 38 mm) and a voltage was selected to supply 500 W power. All sample measurements were recorded in triplicate, plotting averages with error bars showing ± 1 standard deviation.

3 Results and Discussion

3.1 Hydrothermal synthesis of citrate-coated Fe₃O₄ magnetic nanoparticles (MNP-CA)

Citrate-coated magnetic nanoparticles (MNP-CA) were synthesised using a continuous-flow hydrothermal reactor, as described in the experimental section. This method is considered a significant improvement on other commonly reported techniques as it avoids the need for lengthy multi-step batch reactions, organic solvents or air sensitive environments^{22,39–41}. The continuous-flow reactor design is also inherently scalable^{47,48}, providing a sustainable pathway for large-scale production. The formation of magnetite from ammonium ferric citrate is thought to proceed *via* an initial reduction of an amount of Fe(III) to Fe(II) by CO formed in the partial thermal decomposition of ammonium citrate, as has been previously suggested⁵². The reduction of Fe(III) could alternatively occur via the oxidation of citrate. Both Fe(III) and Fe(II) then undergo hydrolysis on reaction with water, before a dehydration precipitating out the metal oxide (Fe₃O₄)⁵³. A simplified hypothetical reaction scheme is therefore proposed⁵⁴:



The nanoparticles produced herein were composed of highly crystalline magnetite (Fe_3O_4) as confirmed via PXRD (Figure 2A), matching the powder diffraction file database (PDF-01-071-6336). The nanoparticles were produced in high purity and exhibit high stability, observed in the PXRD pattern (Figure 2A) showing no oxidation to the less magnetic hematite (α - Fe_2O_3) or maghemite (γ - Fe_2O_3) phases over 8 days (storage at room temperature)⁵⁵. This stability and purity is beneficial for applications relying on the strong magnetic properties such as heating or separation^{56,57}. The size distribution of the nanoparticles was determined by TEM analysis of 302 particles. The resulting histogram is displayed in Figure 2B, showing an average particle size of 19 ± 11 nm. The small size of the nanoparticles cause quantum size effects and large surface areas, resulting in superparamagnetic behaviour⁵⁸, with very high saturation magnetisation (78.3 emu/g) and low remanence (4.2 emu/g). These MNP-CA are comparable in size and shape (Figure 3A,B) to reported citrate-coated Fe_3O_4 nanoparticles, which are synthesised via heated batch co-precipitation methods (19 nm³⁶ 21 nm⁵⁹ 25 nm⁶⁰). Applying the Scherrer equation to the powder diffraction pattern of MNP-CA (Figure 2A) gave a mean crystallite diameter of 29.1 nm, averaged over 6 peaks. This result indicates that each nanoparticle contains a single crystallite with one coherently scattering domain, which is also confirmed in the TEM images showing the diffracting planes in a single nanoparticle (Figure 3C).

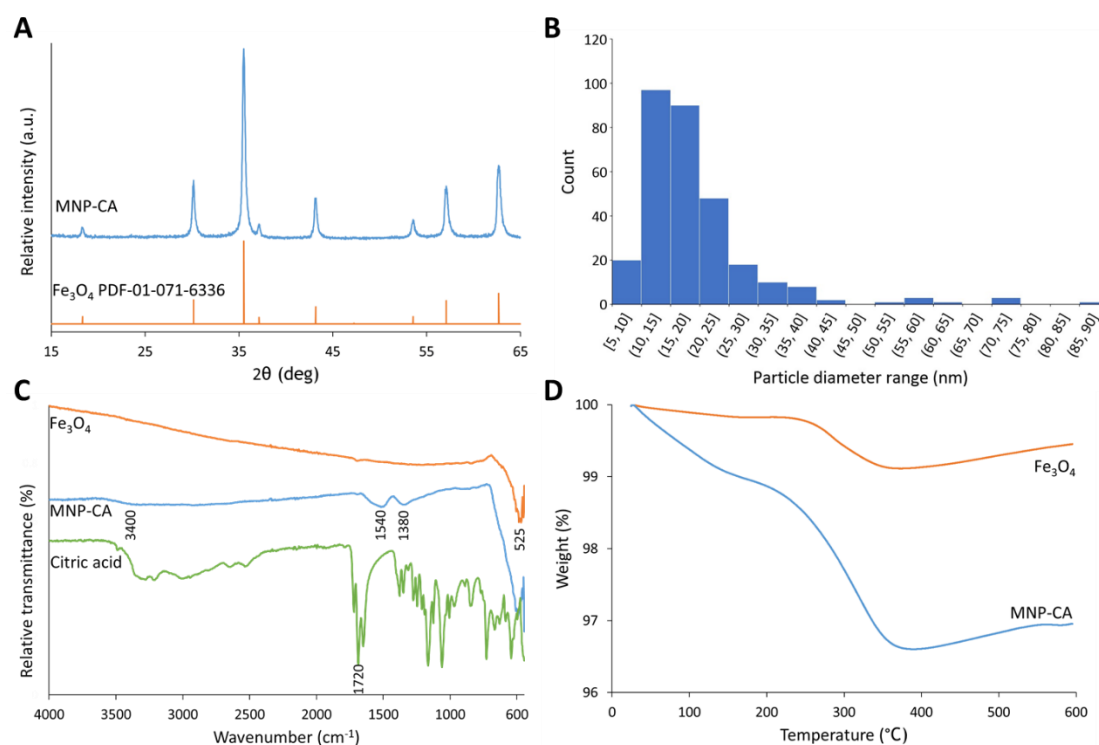


Figure 2: A: PXRD patterns of synthesised MNP-CA and pristine Fe_3O_4 from the powder diffraction file database (PDF-01-071-6336)⁵⁰. B: histogram showing the size distribution of MNP-CA from TEM image analyses. C: FTIR spectra for pristine Fe_3O_4 , synthesised MNP-CA and citric acid. D: graph showing weight loss on heating under N_2 during TGA for pristine Fe_3O_4 and synthesised MNP-CA.

As discussed in the introduction, MNP surface functionalisation is important not just for stability, but also allows the conjugation of other molecules to the MNPs. The presence of a citrate coating on the synthesised MNP-CA was confirmed by FTIR spectroscopy (Figure 2C). The citric acid peak at 1720 cm^{-1} arises from C=O symmetric stretching from the COOH group³⁶. This peak is shifted down to 1540 cm^{-1} in the MNP-CA material owing to chemisorption of the carboxylate on the citrate ion with Fe at the MNP surface^{36,38,61,62}. Complexation likely weakens the C=O bond, introducing partial single bond character and lowering the stretching frequency³⁸. The neighbouring peak at 1380 cm^{-1} in MNP-CA is ascribed to an asymmetric stretch of C-O from the carboxylate group^{36,59,62}, and the broad absorbance at 3400 cm^{-1} from OH groups⁵⁹. The low intensity of these peaks compared to pristine citric acid is common in other reports, and is possibly due to the citrate complexes forming a relatively close-packed layer on the NPs, restricting molecular motion⁶¹. The low intensity of the peaks may also be attributed to the small surface quantities (2.5 wt% by TGA) relative to the bulk MNPs. Finally, the peak at 525 cm^{-1} in MNP-CA and

pristine Fe_3O_4 materials arises from an Fe-O stretching vibrational mode of Fe_3O_4 ^{36,38,59,62}.

The presence of citrate at the surface of the MNPs was further shown by Zeta potential, highlighting the effect of citrate on the MNP properties. A Zeta potential of -47.3 mV was obtained in deionised water (Figure S2, Supplementary Information). The large negative charge arises from electrostatic stabilisation from the strong adsorption of citrate ions on the MNP surface, providing excellent colloidal stability³⁶. The mass fraction of the citrate layer was determined by TGA to be 2.5 wt.% (Figure 2D). MNP-CA contains physically adsorbed (removed at <150 °C, approx. 1 wt.%) and chemically bound (removed up to 375 °C, approx. 1.5 wt.%) citrates. The amorphous citrate coating on the MNPs was also observed as an approximately 1 nm thick layer in the TEM images, see Figure 3C. This result corroborates previous studies of citrate coatings on gold nanoparticles, with layer thicknesses of 0.8-1.0 nm⁶³. The TEM images also show the highly crystalline magnetite regions (Fig 3C, 3D). TEM image analysis of one nanoparticle (Fig 3D) gave an interplanar d-spacing of 0.30 nm (average of 25 measurements), corresponding to the (220) planes at 30 °2 θ ^{64,65}.

Magnetisation of the synthesised MNP-CA was measured by VSM (Figure 5A). The saturation magnetisation reached 78.3 emu/g at 10 kOe, which is considerably higher than other published citrate-coated magnetite nanoparticles, which typically range from 30-60 emu/g^{36-38,61,62}. The higher saturation magnetisation for MNP-CA highlights its high purity as distortion/lattice deformation and micro-strain in nanoparticles can lead to reduced magnetisation⁶⁶. The magnetic and inductive heating properties of Fe_3O_4 nanoparticles are also size-dependant, with the specific absorption rate reported to increase with size up to around 28 nm due to susceptibility then hysteresis loss⁶⁷. The low remanent magnetisation (4.2 emu/g) and intrinsic coercivity (42 Oe) of MNP-CA (Figure 5A) are similar to other reports^{36-38,60}. These low values are advantageous as they result in a high permeability and low energy required to switch the spin directions, beneficial for applications involving magnetic separation, such as in environmental remediation.

High quality citrate-coated magnetite nanoparticles have thus been synthesised in a sustainable and scalable manner, ready for use in a variety of applications such as biomedicine^{33,58}, environmental remediation^{68,69}, catalysis^{70,71} and, as demonstrated in this work, in the synthesis of magnetic framework composites⁷².

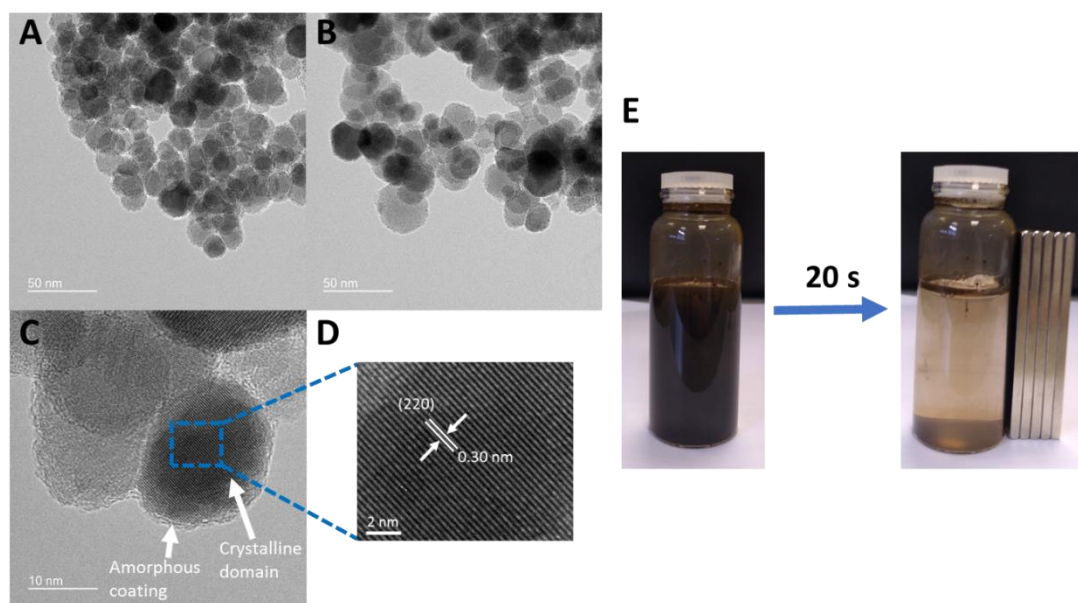


Figure 3: A, B: TEM images showing the approximate size and shape of MNP-CA. B: TEM image showing the crystalline magnetite domains and the amorphous citrate coating on single nanoparticles. D: TEM image showing the highly crystalline magnetite region, with an interplanar d-spacing of 0.30 nm corresponding to the (220) planes at $30^\circ 2\theta$ ^{64,65}. E: 20 s magnetic separation of MNP-CA in deionised water.

3.2 Preparation of magnetic framework composites by encapsulation of nanoparticles

Magnetic framework composites (MFCs) were prepared using the synthesised MNP-CA and a direct growth encapsulation strategy, based on the development of a rapid (10 min) microwave synthesis for MOF UTSA-16(Zn) (Figure S3, Supplementary Information). As previously mentioned, MOF UTSA-16(Zn) was selected for its promise in carbon capture applications due to its high CO₂ uptake and selectivity at relevant partial pressures for post combustion CO₂ capture (0.15 bar), good stability to moisture and acid gases, and low production cost due to the very cheap and abundant starting reagents^{46,73}. A direct growth encapsulation strategy was selected here due to its ease and scalability compared with laborious methods such as layer-by-layer growth²⁵. The direct growth method also still ensures extensive mixing and strong attachment between the components compared to other strategies such as

direct mixing²⁵. The method developed herein, involved adding various concentrations of MNP-CA to the dissolved MOF precursors in water, followed by the addition of an antisolvent (ethanol) and microwave irradiation at 300 W for 10 min at 60 °C (see experimental section for further details). Figure 4A shows the powder diffraction patterns of the composites, where the gradual decrease in the UTSA-16(Zn) peaks (e.g. at 7 and 14 °2 θ) and increase in the MNP-CA peaks (e.g. at 36 and 63 °2 θ) are observed with increasing MNP-CA content. PXRD data also confirm the crystallinity of both the MOF and MNP-CA components in the UTSA16(Zn)@MNP-CA MFCs. The exact quantities of MNP-CA in the MOF, determined using saturation magnetisation measurements²² (Figure 5A), were between 2.6-18.7 wt%. This range is similar to other reported MFCs, including 0.1-7.8 wt% Fe₃O₄ in Mg-MOF-74⁷⁴, 1-10 wt% MgFe₂O₄ in Al-fumarate⁷⁵, 1.3-7.3 wt% Fe₃O₄ in PCN-250⁷⁶, 0.1-15.0 wt% Fe₃O₄ in Co-MOF-74⁷⁷ and 2.0-4.1 wt% MgFe₂O₄ in UiO-66²¹.

The impact of increasing MNP-CA content in the UTSA-16(Zn)@MNP-CA MFCs on yield and CO₂ adsorption (measured gravimetrically by TGA⁷⁸) is shown in Figure 4B. It should be noted that although there is a decrease in CO₂ capacity from 3.4 to 2.8 mmol/g with increasing MNP-CA content (as expected, owing to MNP-CA not adsorbing CO₂), there was no decrease in the adsorption capacity of the MOF when accounting for the MNP-CA mass in the various MFCs. These results indicate that MNP-CA has no detrimental effect on the MOF synthesis (as crystal structure is maintained) or ability of the MOF to adsorb CO₂, which could potentially arise from pore-blocking^{28,79}. The CO₂ capacities observed for UTSA-16(Zn) and the MFCs were similar to those reported elsewhere for pristine UTSA-16(Zn) (3.5 mmol/g)⁷³ and other high performing MOFs/MOF composites^{80,81}, though were not as high as the absolute maximum reported value for pristine UTSA-16(Zn) (4.7 mmol/g)⁴⁶. However, a balance must be struck between how the material is prepared and its performance if considering industrial viability. Compared to the 4.7 mmol/g literature method, the synthesis time for preparing the pristine MOF (and associated MFCs) was reduced by a factor of 24, the washing/solvent exchange was reduced from 14 washes over 3 days to 3 washes over 1 h, diethyl ether was removed as a washing solvent, all anhydrous/dry washing solvents were replaced with standard

commercial solvents, and 90 °C vacuum drying activation was reduced to 50 °C without a vacuum. These changes resulted in a significant improvement towards the sustainability and scalability of MOF synthesis, especially with regards to the washing/solvent exchange and activation procedure. The additional advantage of the MFCs is the magnetic induction heating capability for rapid and low-energy regeneration.

The overall product yield benefited from the presence of MNP-CA (Figure 4B), as an increase from 77% (pristine MOF) to 81-83% (MFCs, 0.8-0.9 g) was observed. This increase in yield may result from higher localised temperatures around MNP-CA due to enhanced interactions with the microwave field^{82,83}. The impact of increasing MNP-CA content in the MFCs on N₂ adsorption isotherms and apparent BET surface area was also evaluated (Figure 4E,F). The adsorption isotherms in Figure 4E of the UTSA-16(Zn) and MFCs match those found in the literature for the MOF, showing a type 1 isotherm due to the microporous structure⁴⁶. The surface areas are also similar to those previously reported for the MOF^{46,73}, though decreased more than expected purely from the mass contribution of the MNP-CA, from 741 m²/g without any MNP-CA down to 551 m²/g at 18.7% MNP-CA. The trendline between different MNP-CA concentrations in the MFCs was also less clear than observed with CO₂ adsorption capacity (Figure 4F; Figure S4, Supplementary Information). This result highlights the importance of testing the sorption capacity of new materials and composites for sorption applications, rather than depending on BET surface area as a sorption capacity analogue for comparisons between materials. Further considerations and guidance for using the BET method for surface area measurements of MOFs have also been recently reported^{84,85}.

The impact of regeneration temperature on CO₂ capacity was investigated, in order to maximise the efficiency of the sorbent regeneration process (releasing the adsorbed CO₂ for sorbent reuse). Figure 4C displays results between 25 and 120 °C for one of the MFCs, UTSA-16(Zn)@MNP-CA (18.7%). The graph shows the average CO₂ adsorption capacity over 4 adsorption-desorption cycles at each regeneration temperature. The error bars show the decrease in capacity between the first (top error bar) and forth (bottom error bar) cycle. Increasing regeneration temperatures

result in larger CO₂ adsorption capacities as expected, with the trend showing a steeper increase at lower temperatures (up to 50 °C), which slowly levels off at higher temperatures (up to 120 °C). The decrease in capacity over 4 cycles at each regeneration temperature is also largest at the lower regeneration temperatures (up to 40 °C). This drop in capacity is likely due to insufficient energy being supplied in each desorption step to remove all the adsorbed CO₂ from the previous adsorption step. These are important considerations for industrial process designs, where energy costs from higher heating must be balanced against the requirement for more material to capture the same amount of CO₂, or faster adsorption-desorption cycles¹⁶. This balance will likely vary for different applications and scales, depending on availability and recoverability of heat, capture unit size restraints, and other factors. Overall, the regeneration temperatures required for the UTSA-16(Zn)@MNP-CA (18.7%) MFC were remarkably low (50-60 °C) compared with the temperatures required for regeneration of other adsorbents, including carbon-based materials (120-230 °C)⁸⁶, zeolites (200 °C)⁸⁷ and other MFCs (130-145 °C)²². For UTSA-16(Zn)@MNP-CA (18.7%), 60 °C was selected as a representative low regeneration temperature to test the CO₂ capacity over 12 cycles of adsorption-desorption (Figure 4D). No decrease in the CO₂ adsorption capacity over the 12 cycles was observed (cycle 1: 2.58 mmol/g, cycle 12: 2.59 mmol/g). It is also worth noting here that UTSA16(Zn)@MNP-CA MFCs are all thermally stable up to 250 °C, which is the same as the pristine MOF, indicating that MNP-CA has no detrimental effect on the thermal stability of UTSA-16(Zn) (Figure S5, Supplementary Information).

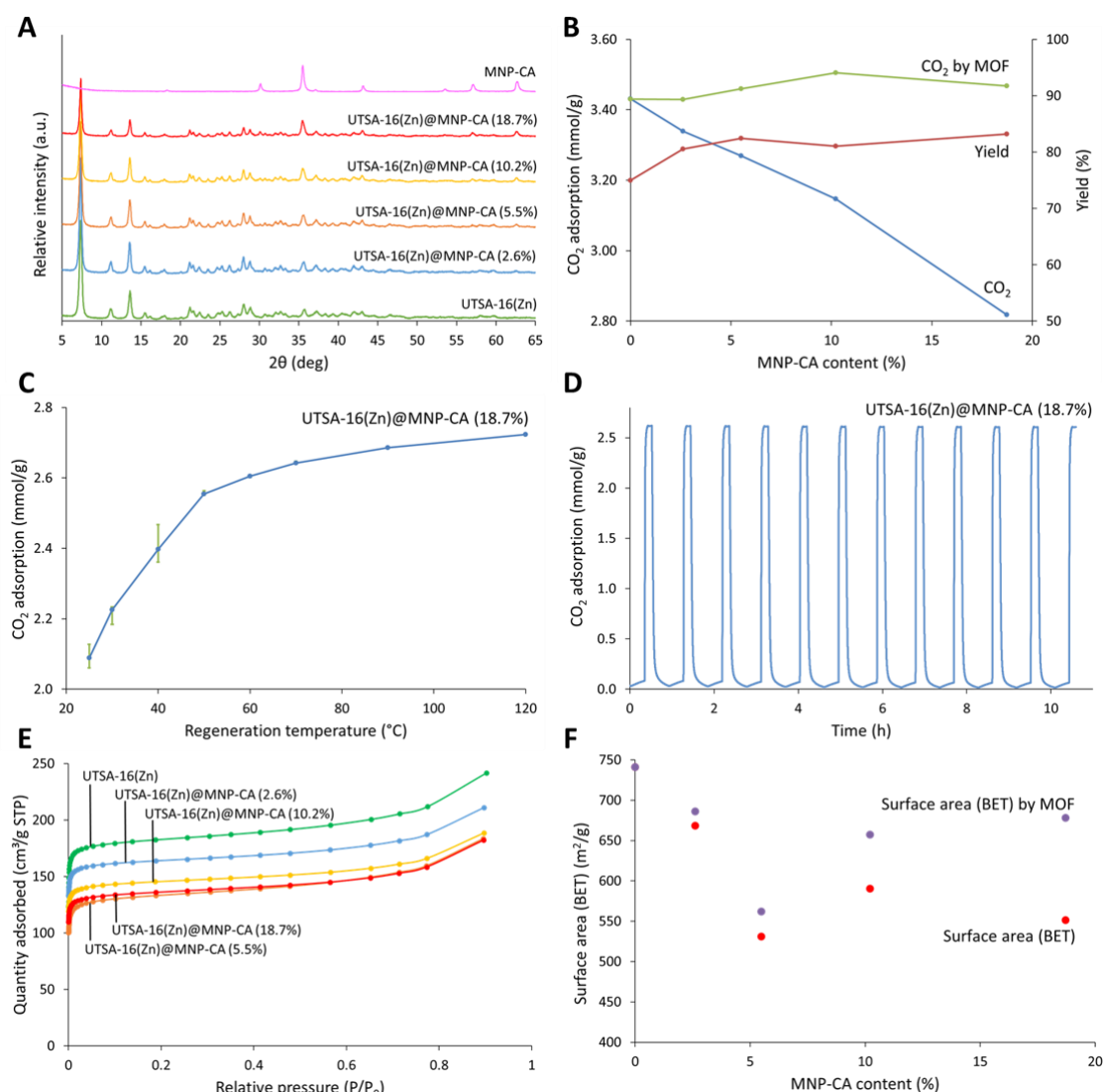


Figure 4: A: powder X-ray diffraction patterns between 5 and 45 °2 θ of pristine UTSA-16(Zn), MNP-CA and UTSA-16(Zn)@MNP-CA MFCs containing various quantities of MNP-CA. B: CO₂ adsorption capacity and product yield of MFCs plotted against MNP-CA content. CO₂ adsorption of the MOF is plotted by subtracting the mass contribution from MNP-CA. C: regeneration temperature plotted against CO₂ adsorption capacity for UTSA-16(Zn)@MNP-CA (18.7%), results are averages of 4 repeat cycles. Error bars show the decrease in capacity between the first and fourth cycle. D: CO₂ adsorption capacity for UTSA-16(Zn)@MNP-CA (18.7%) over 12 adsorption-desorption cycles. Regeneration was performed at 60 °C. E: N₂ adsorption isotherms of UTSA-16(Zn) and UTSA-16(Zn)@MNP-CA MFCs, measured at 77K. F: Apparent BET surface area (Rouquerol)⁸⁸ plotted against MNP-CA content for UTSA-16@MNP-CA MFCs. Surface area 'by MOF' was determined by subtracting the mass contribution from MNP-CA.

As previously introduced, the primary benefit of forming magnetic composites with MOFs for carbon capture applications is the ability of the material to undergo rapid and energy-efficient induction heating for CO₂ regeneration. Induction heating is the process by which energy is transferred from an H-field applicator to a material placed in the magnetic field. Heating occurs in magnetic conductive materials through both resistance to induced eddy currents and losses from the magnetisation-

demagnetisation cycles in magnetic domains⁸⁹. Therefore, the magnetisation and induction heating properties of UTSA16(Zn)@MNP-CA MFCs were measured (Figure 5, Table 1). The results for magnetisation of the MFCs as measured by VSM were compared to pristine MNP-CA. Increasing concentrations of MNP-CA resulted in increasing saturation (2.0-14.7 emu/g) and remanent (0.2-1.2 emu/g) magnetisations, with intrinsic coercivity remaining roughly constant between samples (50 Oe). The saturation magnetisation values for the MFCs cover a similar range to the 1.5-4 emu/g reported for MgFe_2O_4 in UiO66²¹, 0.1-3.9 emu/g for Fe_3O_4 in Mg-MOF-74⁷⁴ and 3.1-18.4 emu/g for Fe_3O_4 in PCN-250⁷⁶. The low relative values of the remanent magnetisations compared to saturation magnetisations, and the low intrinsic coercivities, are again advantageous for applications involving magnetic separation, as mentioned earlier for the pristine MNP-CA. There was an approximate direct proportionality between the saturation magnetisation of UTSA16(Zn)@MNP-CA MFCs and the temperature increase observed over a 30 s period of induction heating at 500 W, magnetic field: 164 A/m (factor of 7-8.4).

These magnetisation and heating results highlight another significant consideration for industrial process design, where heating/cycle durations can be balanced against concentration of MNP-CA in the MFCs (i.e. a higher concentration of MNP-CA in the MFCs results in a lower CO_2 capacity, but a shorter heating/cycle time for regeneration. E.g. UTSA16(Zn)@MNP-CA (18.7%): CO_2 capacity of 2.8 mmol/g, reaches 60 °C in 8 s heating. UTSA16(Zn)@MNP-CA (10.2%): CO_2 capacity of 3.1 mmol/g, reaches 60 °C in 15 s heating). A higher power of induction heating would also result in a shorter heating/cycle time, but with a higher energy requirement. Figure 5B shows the induction heating profiles of the UTSA16(Zn)@MNP-CA MFCs, demonstrating their ability to reach the temperatures required for regeneration (i.e. 60 °C) in only 8-30 seconds, even at low MNP-CA concentrations (5.5-18.7%) and low induction heating power (500 W). Typical regeneration times for alternative adsorbents such as activated carbon and zeolites are reported to be around 20-40 min to achieve >90% CO_2 recovery, using conventional or microwave heating^{90,91}, and other MFCs have reported regeneration times as low as 4-11 min via magnetic induction heating^{21,22,75}.

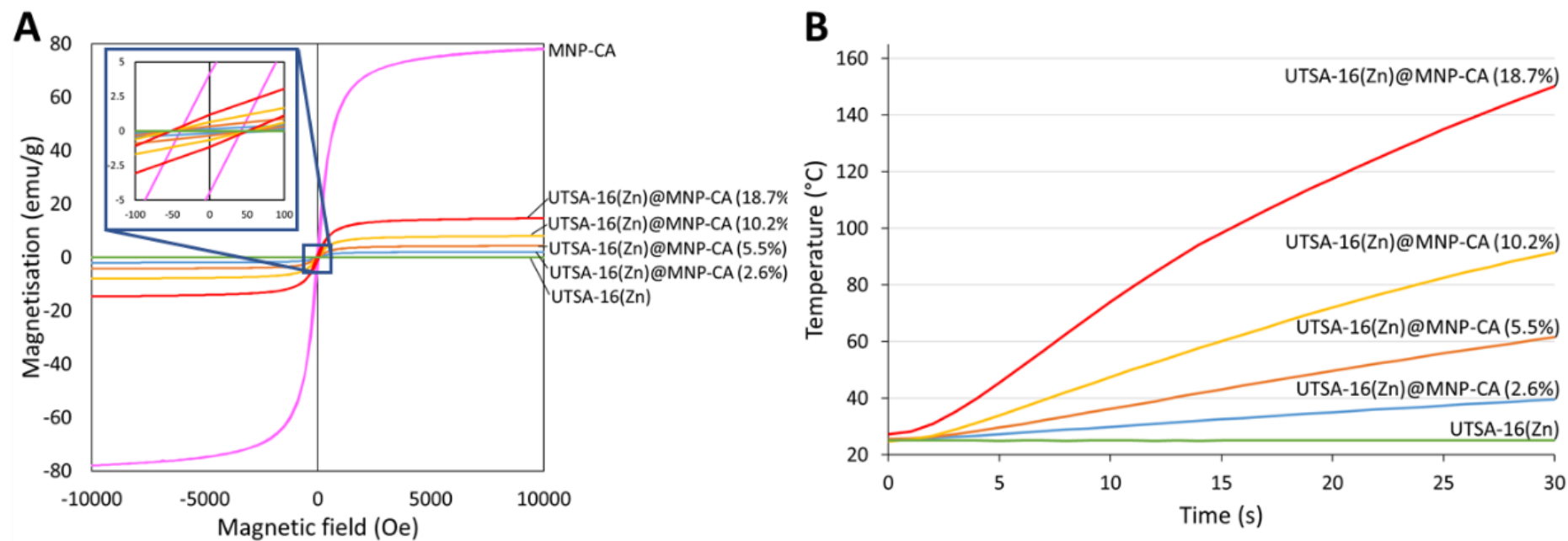


Figure 5: A: VSM measurements of UTSA-16(Zn), UTSA-16(Zn)@MNP-CA MFCs, and MNP-CA taken at room temperature with a field strength up to 10 kOe. B: Induction heating temperature plotted against time for UTSA-16(Zn) and UTSA-16(Zn)@MNP-CA MFCs at 500 W over 30 s.

Table 1: Magnetisation properties and induction heating temperature increase for UTSA-16(Zn), UTSA-16(Zn)@MNP-CA MFCs, and MNP-CA.

Sample	Saturation magnetisation (emu/g, M_{sat})	Remanent magnetisation (emu/g, M_r)	Intrinsic coercivity (Oe, H_c)	Temperature increase over 30 s heating ($^{\circ}\text{C}$, 500 W)
UTSA-16(Zn)	0.0	0.0	0	0
UTSA-16(Zn)@MNP-CA (2.6%)	2.0	0.2	50	14
UTSA-16(Zn)@MNP-CA (5.5%)	4.3	0.3	50	36
UTSA-16(Zn)@MNP-CA (10.2%)	8.0	0.7	50	67
UTSA-16(Zn)@MNP-CA (18.7%)	14.7	1.2	50	123
MNP-CA	78.3	4.2	42	232*

* MNP-CA heated very rapidly so was only heated for 8 s (not in triplicate)

To examine the distribution of MNP-CA within UTSA-16(Zn) for the UTSA-16(Zn)@MNP-CA MFCs, TEM and SEM imaging with EDX elemental analyses were conducted on UTSA-16(Zn)@MNP-CA (18.7%). The average particle size of the MFC was determined by SEM image analysis on 100 particles, showing a mean diameter of 55 ± 16 nm (standard deviation). Results of the TEM analysis are shown in Figure 6. UTSA-16(Zn)@MNP-CA (18.7%) was sonicated to break down the powder into primary agglomerates, where it was observed that good mixing between the MOF and the MNP-CA had occurred, i.e. primary agglomerates contained MOF and MNP-CA nanoparticles bound together. This result was further corroborated by SEM and EDX analyses, where Zn from UTSA-16(Zn) (green) and Fe from MNP-CA (pink) could be clearly seen (Figure S6, Supplementary Information). The uniform distribution of MNP-CA and UTSA-16(Zn) nanoparticles in primary agglomerates meant that a high wt.% MOF loading (81-97%) could be used in the MFCs, whilst still ensuring effective induction heating throughout the material. These composite structures differ from the thin MOF layers grown on individual nanoparticles (core-shell structures) frequently observed for other MFCs in the literature, such as HKUST-1 on Fe_3O_4 ^{40,45} or ZIF-8 on Fe_3O_4 ⁴¹. These core-shell structures are usually prepared by lengthy layer-by-layer syntheses methods, with much lower wt.% MOF loadings in the composites^{40,45}. Although they demonstrate efficacy in catalysis applications⁴⁰, the low MOF loadings would result in low gravimetric capacities in adsorption applications. The MNP-CA and UTSA-16(Zn) nanoparticle primary agglomerates also

differ in morphology from MFCs synthesised by lengthy direct-growth methods, where nanoparticles are embedded in large MOF crystals, such as MgFe_2O_4 in Mg-MOF-74²² or Fe_3O_4 in Co-MOF-74⁷⁷ prepared via 15 h and 2.5 day syntheses, respectively.

This work shows that MFCs containing UTSA-16(Zn) and MNP-CA can be synthesised in a facile, low-cost, rapid, and sustainable manner, with varying concentrations of MNP-CA for applications with different magnetic property requirements. The high CO_2 adsorption capacity (3.4-3.5 mmol/g) of the MOF in the MFCs was unaffected by the incorporation of MNP-CA, and the resulting MFCs showed highly effective thermal regeneration at temperatures as low as 60 °C, which could be attained in seconds via the energy efficient induction heating process.

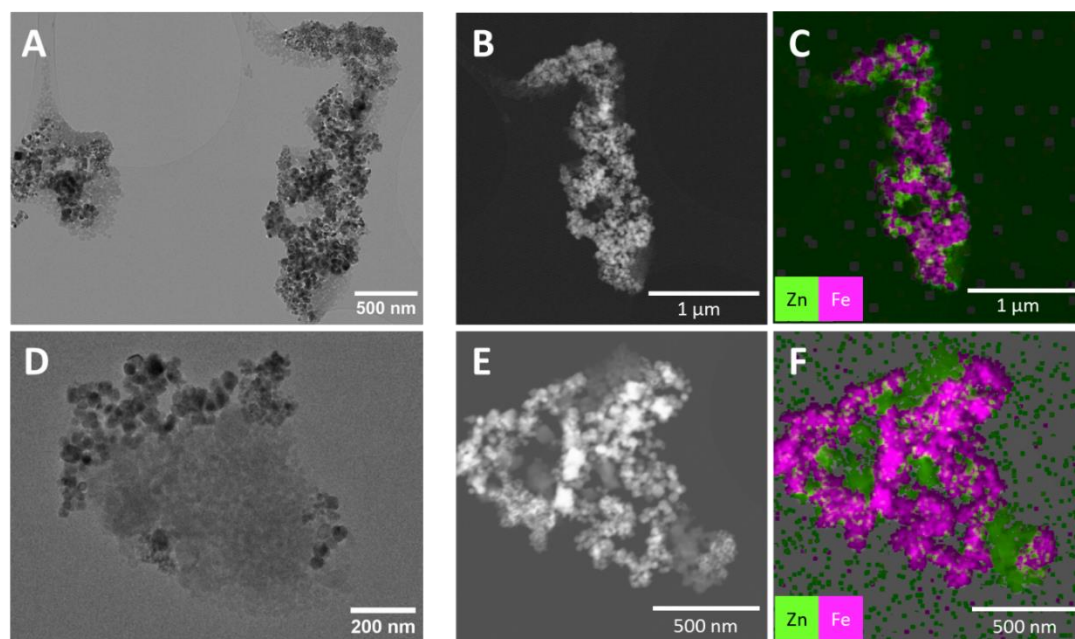


Figure 6: A,D: TEM images of agglomerate particles of MFC UTSA-16(Zn)@MNP-CA (18.7%), containing both UTSA-16(Zn) and MNP-CA nanoparticles. B,C,E,F: TEM EDX images of the MFC showing the distribution of Zn (green) from UTSA-16(Zn) and Fe (pink) from MNP-CA in the agglomerate particles.

4 Conclusions

In this work, the synthesis, characterisation, and testing of sustainable and novel UTSA-16(Zn)@MNP-CA MFCs for post-combustion carbon-capture applications is described. Firstly, a single-step and scalable continuous-flow hydrothermal method was developed for producing citrate-coated Fe_3O_4 nanoparticles (MNP-CA), mean

diameter: 19 ± 11 nm. MNP-CA showed a very high saturation magnetisation (78 emu/g) compared to previously published alternatives, due to its very high purity and crystallinity. This method not only avoids the use of harsh and lengthy batch synthesis conditions, but also citrate coated the nanoparticles *in-situ*, removes the need for additional functionalisation steps.

Next, various concentrations of MNP-CA (2.6-18.7 wt%) were incorporated into UTSA-16(Zn) MOF *via* a rapid 10 min 60 °C microwave direct-growth synthesis to produce innovative UTSA-16(Zn)@MNP-CA MFCs (magnetisation: 2-15 emu/g). The yield of the MFCs was shown to slightly benefit from MNP-CA incorporation compared to the pristine MOF (81-83% for the MFCs, 77% for the pristine MOF). TEM and XRD analyses revealed that the MFCs contain agglomerates of bound crystalline MOF and MNP-CA nanoparticles, which maintain high CO₂ adsorption capacities (2.8-3.3 mmol/g) and recyclability, with no loss of MOF CO₂ capacity with increasing MNP-CA loading in the MFCs. Regeneration temperature had an impact on both total CO₂ capacity and capacity loss over multiple cycles. Remarkably low temperatures and short timescales were sufficient for regeneration of the MFCs compared with other solid adsorbents. The MFCs also exhibited the desired rapid magnetic induction heating (e.g. 60 °C in 8 seconds), overcoming the challenge of rapid and low energy thermal CO₂ regeneration in CO₂ capture applications.

These MFCs have thus demonstrated leading adsorption profiles and regeneration heating capabilities for CO₂ release, while being produced in a scalable and sustainable manner from cheap and widely available materials. The combination of these properties represents a significant advancement in the field of MOFs/MFCs for CO₂ capture, making the next step toward industrial application. The MFCs should next be produced and tested on a pilot-scale carbon capture unit prior to industrial use. In addition, since the MNP-CA and the MFC synthesis method could be applied to other MOFs, a variety of sustainable MFCs could also be synthesised for impact in wide-reaching applications.

5 Author contributions

John Luke Woodliffe: Conceptualization, Formal Analysis, Validation, Funding Acquisition (via Henry Royce Institute), Investigation, Methodology, Writing – Original Draft, Writing – Review & Editing, Visualization. Amy-Louise Johnston: Investigation, Writing – Original Draft, Visualization. Michael Fay: Investigation. Rebecca Ferrari: Conceptualization, Writing – Review & Editing. Rachel L Gomes: Writing – Review & Editing. Ed Lester: Resources, Writing – Review & Editing. Ifty Ahmed: Conceptualization, Supervision, Writing – Review & Editing. Andrea Laybourn: Conceptualization, Project Administration, Supervision, Writing – Review & Editing, Funding Acquisition (EPSRC CDT).

6 Conflicts of interest

There are no conflicts to declare.

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Supplementary Information

Rapid microwave synthesis of sustainable magnetic framework composites of UTSA-16(Zn) with Fe₃O₄ nanoparticles for efficient CO₂ capture

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Citrate-coated Fe_3O_4 nanoparticles (MNP-CA)

Size distribution of MNP-CA agglomerates

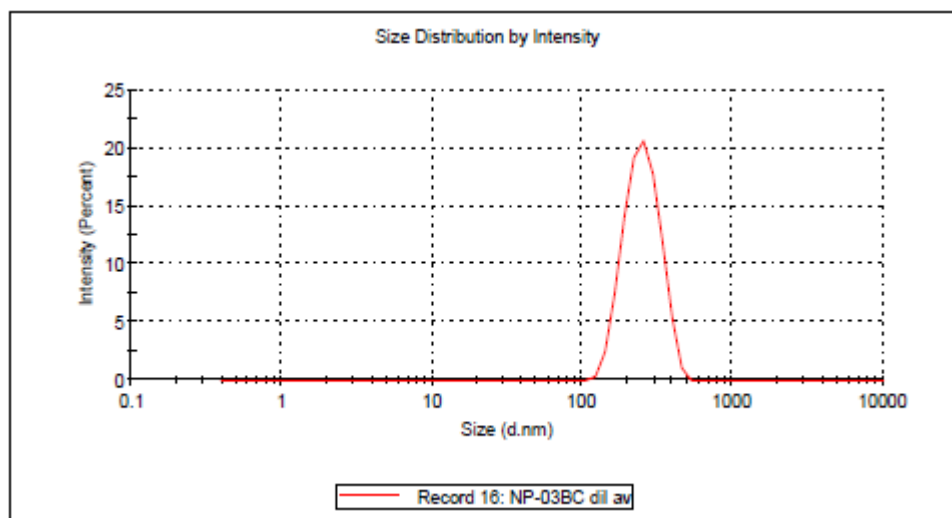


Figure S1: Size distribution by intensity measured by dynamic light scattering, showing the hydrodynamic size of MNP-CA agglomerates.

Zeta potential of MNP-CA in water

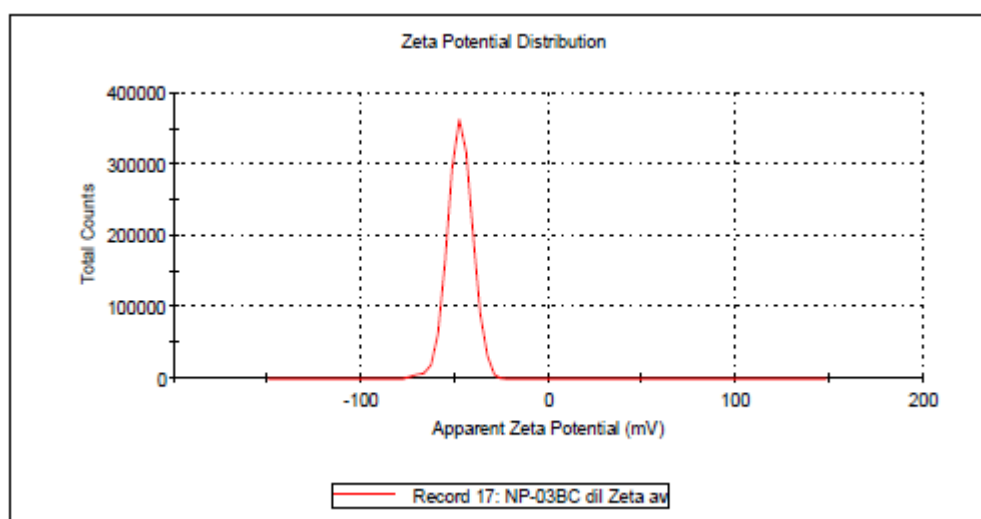


Figure S2: Zeta potential distribution for MNP-CA dispersed in water.

Synthesis and CO₂ adsorption of pristine MOF UTSA-16(Zn)

Synthesis of UTSA-16(Zn)

Zn(AcO)₂·2H₂O (0.439 g, 2 mmol), citric acid monohydrate (0.420 g, 2 mmol) and KOH (0.34 g, 5.2 mmol) were dissolved in H₂O (5 mL) in a 35 mL microwave vial. EtOH (5 mL) was added and stirred (10 min) before the vial was sealed and irradiated under autogenous pressure with stirring at a maximum forward power of 300 W (commercial CEM discover microwave reactor, dynamic mode, T = 25-150 °C, t = 0-60 min). After the reaction, the vial was cooled in the microwave cavity with air, then the product was collected by washing out the vial with H₂O:EtOH 1:1 (20 mL) followed by centrifugation. The product was then washed by centrifuge with MeOH (3 x 30 mL, 4200 RPM, 20 mins) before drying in an oven (50 °C, >4 h).

Synthesis optimisation and CO₂ adsorption of UTSA-16(Zn)

The synthesis of UTSA-16(Zn) has been reported via a solvothermal route (120 °C for 2 days)¹ or more rapidly at 90 °C for 4 h using microwave heating.² In this work we further optimised the preparation of UTSA-16(Zn) before investigating its synthesis in the presence of MNP-CA for the production of MFCs. Figure S3A shows the washing procedure used to activate the MOF post-synthesis. Previous work used anhydrous MeOH and Et₂O with 2 days of soaking². For large scale applications the use of Et₂O is strongly discouraged due to safety concerns around its volatility and flammability³. The use of anhydrous solvents and 2 days of soaking and replenishing would also be limiting at scale, due to the cost and volumes of solvents required, and the timescales for soaking. Figure S3A shows the washing and activation of the MOF without anhydrous solvents. Removing the Et₂O solvent wash, and 2 days of soaking, had no effect on CO₂ adsorption performance. An optimised reduced washing procedure of 3 x 30 mL MeOH was therefore selected for future batches. It should be noted that in this study, CO₂ adsorption was measured using the more efficient and time-saving evaluation of gravimetric gas uptake using TGA⁴. Using non-anhydrous solvents and a gravimetric test set-up, the value of CO₂ adsorption obtained using the previously mentioned published microwave method (90 °C, 4 h)² was 3.5 mmol/g, so this value was used for comparisons during method optimisation.

To maximise the energy and time efficiency of the synthesis, the reaction temperature and duration were optimised using a microwave method. Although slight improvements to yield and CO₂ adsorption capacity were made with longer durations and higher temperatures, most progress made was only up to 60 °C and in the first 10 minutes (Figure S3B,C). These results show for the first time that UTSA-16(Zn) MOF could be synthesised with a high yield (0.31 g, 77%) in a rapid and energy-efficient manner (60 °C, 10 min microwave synthesis). Microwave-synthesised UTSA-16(Zn) exhibits a CO₂ adsorption capacity of 3.4 mmol/g (Figure S3B) and apparent BET surface area of 741 m²/g (Figure S3A). These results further support our previous reports of MOF synthesis using selective microwave heating^{5–9}.

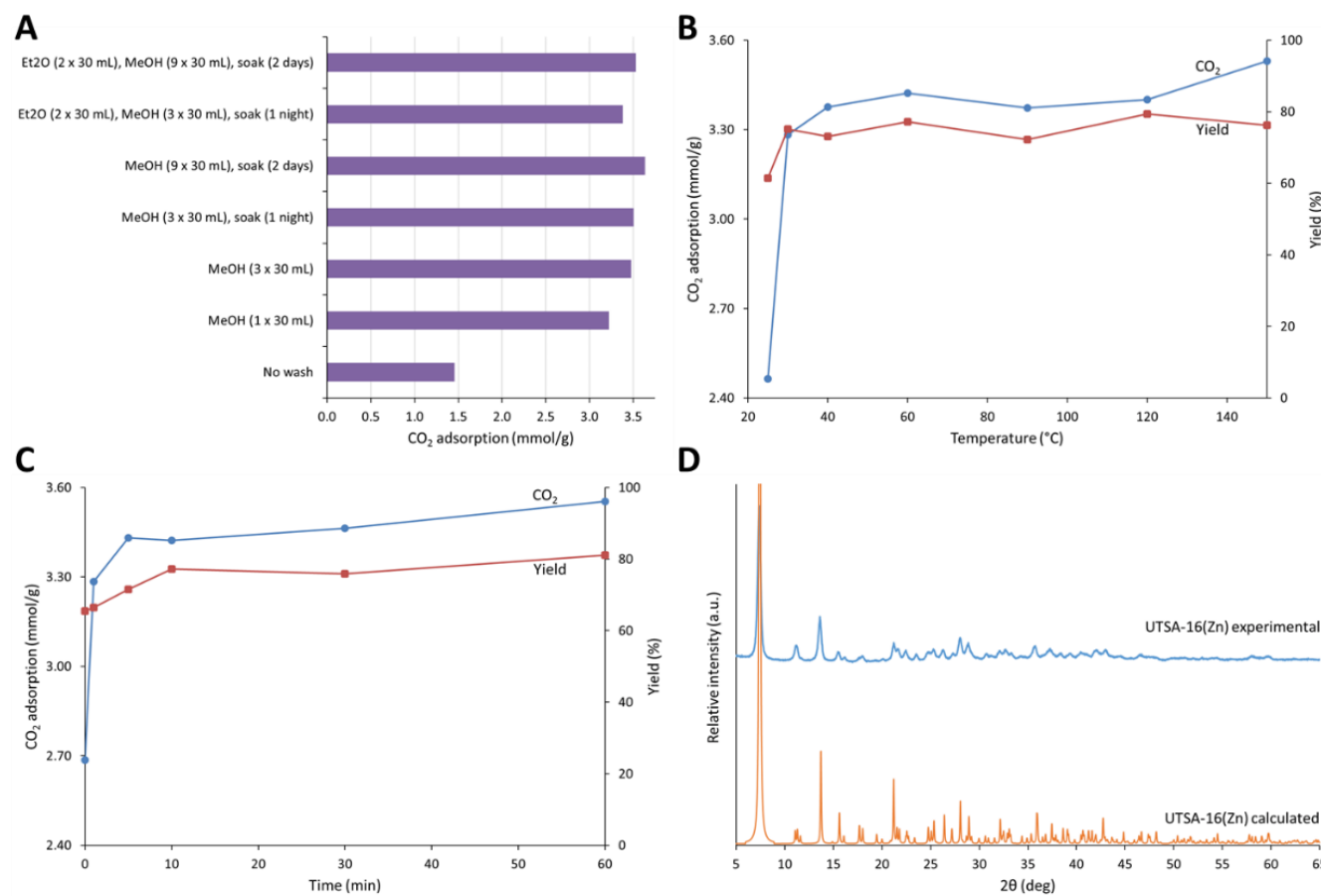


Figure S3: All CO₂ adsorption measured gravimetrically by TGA. A: a comparison of washing and activation techniques for UTSA-16(Zn) produced at 90 °C for 4 h. B: CO₂ adsorption against temperature for UTSA-16(Zn) produced at 10 min. C: CO₂ adsorption against time for UTSA-16(Zn) produced at 60 °C. D: PXRD patterns of UTSA-16(Zn), calculated using Mercury software¹⁰ and experimental produced at 60 °C for 10 min. All UTSA-16(Zn) materials were synthesised using microwave heating.

UTSA-16(Zn)@MNP-CA magnetic framework composites (MFCs)

BET surface area and CO₂ adsorption analyses comparison of MFCs

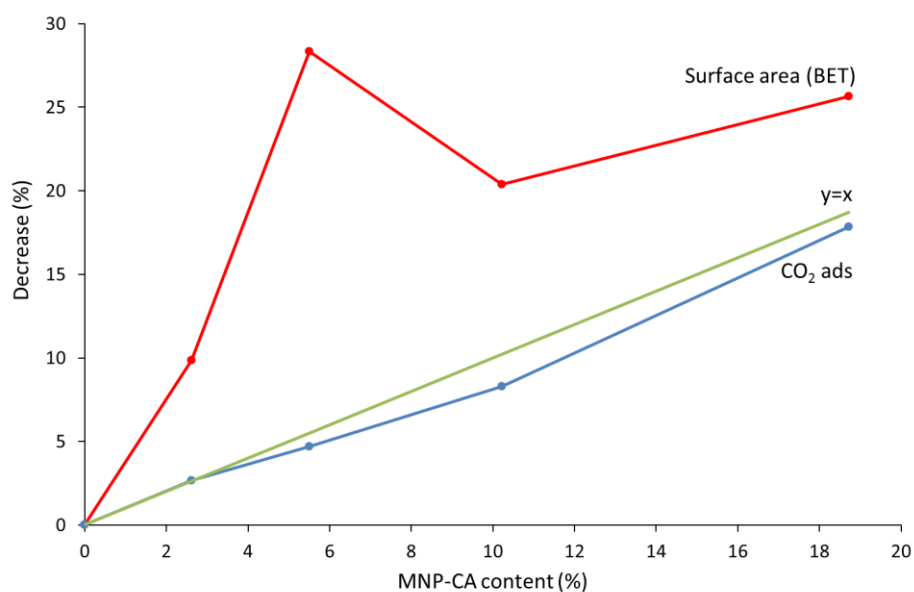


Figure S4: Decrease in CO₂ adsorption capacity and apparent BET surface area plotted against MNP-CA content for UTSA-16@MNP-CA MFCs. A line for $y=x$ represents MNP-CA content for comparison.

Thermal decomposition of MFCs

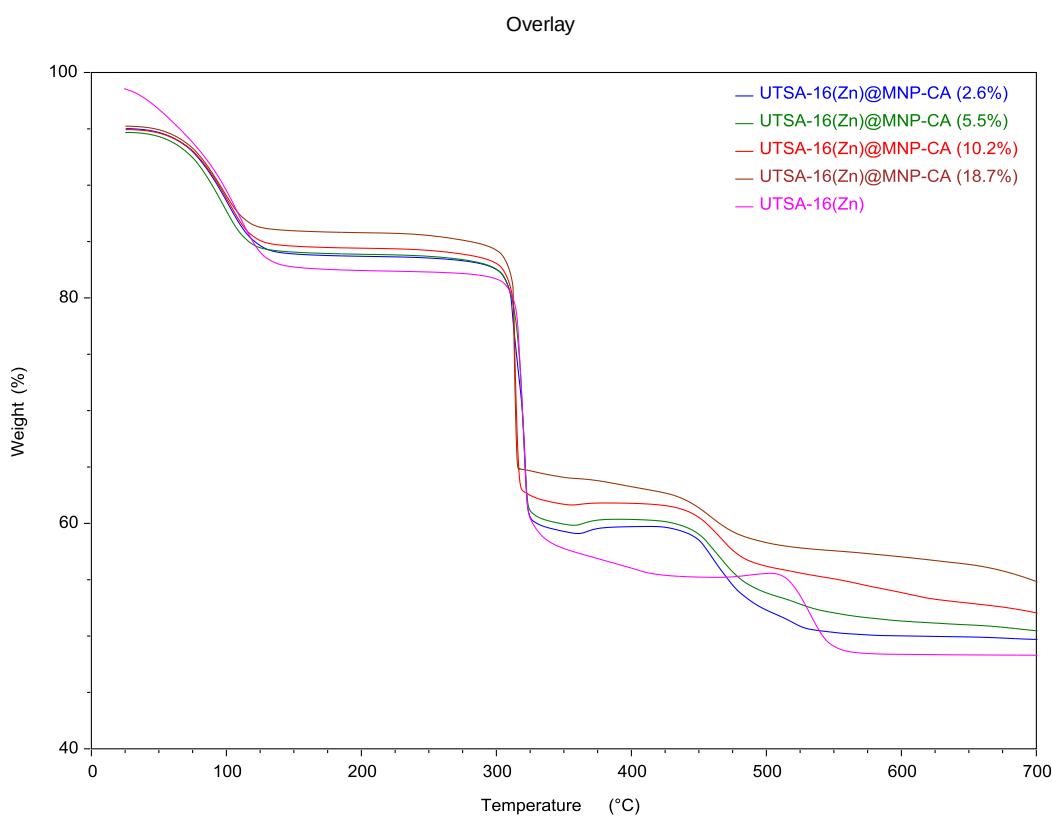


Figure S5: TGA thermograms showing thermal decomposition of UTSA-16(Zn)@MNP-CA with various loadings of MNP (see legend) and pristine UTSA-16(Zn). Measurements conducted under air at a ramp rate of 10 °C/min.

SEM and EDX image analyses of MFCs

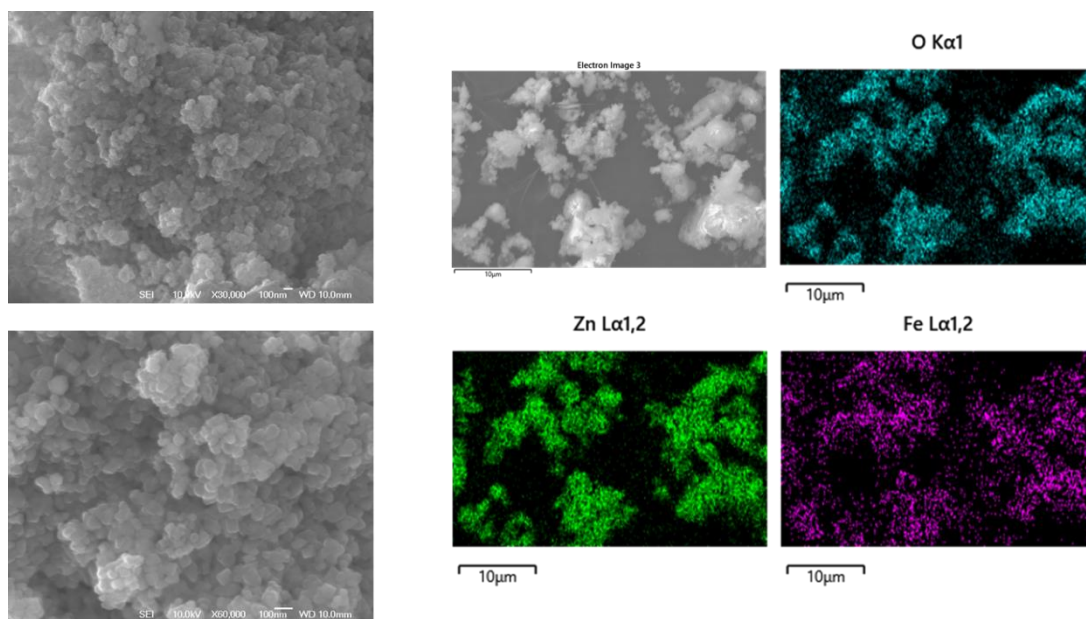


Figure S6: Left: SEM images of UTSA-16(Zn)@MNP-CA (18.7%). Right: elemental mapping by EDX of the same material, Zn (green) showing the distribution of the UTSA-16(Zn) MOF and Fe (pink) showing the distribution of the Fe_3O_4 magnetic nanoparticles. Blue shows the distribution of O atoms, present in both UTSA-16(Zn) and Fe_3O_4 .

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Appendix 4

Continuous flow synthesis of MOF UTSA-16(Zn), mixed-metal and magnetic composites for CO₂ capture – toward sustainable and scalable manufacture

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Target journal: ACS Sustainable Chemistry & Engineering (2023)

Statement of contribution

- Woodliffe J. L.: literature review/research, laboratory experiments, analysis and characterisation, creation of figures/graphs/tables, writing original draft, review & editing, topic & idea (continuous flow synthesis of UTSA-16(Zn), UTSA-16(Zn,Mg) and MFCs) conceptualisation
- Hussein O.: contribution to analysis (VSM)
- Lester E.: review & editing (not yet included for this version)
- Ferrari B.: review & editing (not yet included for this version), topic conceptualisation
- Ahmed I.: review & editing, topic conceptualisation
- Laybourn A.: review & editing, topic conceptualisation

Continuous flow synthesis of MOF UTSA-16(Zn), mixed-metal and magnetic composites for CO₂ capture – toward sustainable and scalable manufacture

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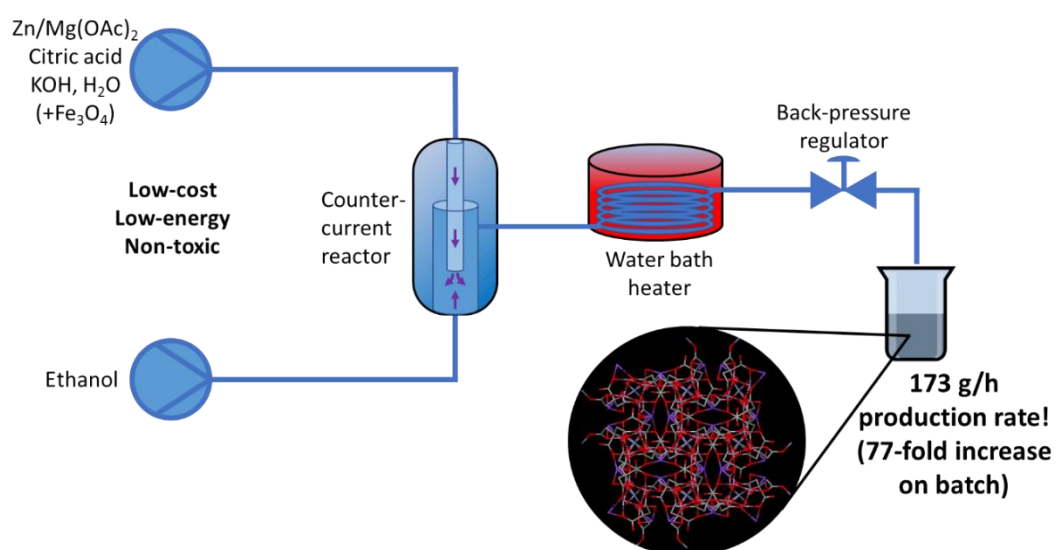
Keywords: metal-organic framework, mixed-metal, magnetic framework composite, magnetic nanoparticles, induction heating, MISA, carbon capture, continuous flow, adsorption, life-cycle analysis

Abstract

UTSA-16(Zn) is a zinc and citrate based metal-organic framework (MOF) with highly promising performance for CO₂ capture. However, no scalable synthesis method has yet been found for this MOF, preventing its transition to industrial application. Herein we report the first scalable continuous flow synthesis for UTSA-16(Zn), demonstrating a significantly higher production rate (173 g/h) compared to previous batch methods (77-fold increase). Sustainability of synthesis was maximised using low-cost non-toxic reagents and a low-energy flow reactor operating at atmospheric pressure. Chemical (reactant ratios, Zn/Mg mixed-metal) and process parameters (solvent pump ratio, flow rate, temperature) were optimised to continuously produce UTSA-16(Zn) with a high CO₂ adsorption capacity (up to 3.8 mmol/g) and conversion yield (up to 66%). Pristine MOFs are typically thermally insulating, making thermal regeneration challenging. To overcome this limitation, magnetic nanoparticles can be embedded within the MOF structure, enabling rapid and energy efficient regeneration using induction heating. Here, citrate-coated Fe₃O₄ magnetic nanoparticles (MNP-CA) were successfully incorporated into the flow synthesis of

UTSA-16(Zn) to form UTSA-16(Zn)@MNP-CA magnetic framework composites (MFCs), representing the highest production rate reported of any MFC to date (152 g/h c.f. 13 g/h for $\text{MgFe}_2\text{O}_4@\text{UiO-66-NH}_2$). The UTSA-16(Zn)@MNP-CA MFCs demonstrated rapid heating under a magnetic field (26-150 °C over 60 s). The flow method developed herein can also be widely applicable for scalable manufacture of other MOFs and MFCs, supporting their broader transition towards industrial applications.

Graphical abstract



1 Introduction

Achieving net-zero greenhouse gas emissions is a key priority for governments and industries worldwide. Urgent action is required to meet these targets and minimise the on-going devastating impacts of climate change. To reach these targets, CO₂ capture has been shown play a vital role¹. CO₂ can be captured at its largest sources, power plants, through post-combustion capture facilities, which can be retrofitted into existing plants². Currently, amine technologies have been used, however, these suffer from solvent decomposition/degradation and have very high energy requirements, limiting widescale deployment and use³. Porous solid adsorbents are considered an energy-efficient alternative for CO₂ capture⁴, with significantly reduced energy for CO₂ separation and material regeneration for reuse⁵.

Metal-organic frameworks (MOFs) are a class of porous materials containing metal ions/clusters and organic linkers⁶. They are of particular interest in CO₂ capture applications due to their tailorable structures with high capacities and selectivities for CO₂⁷. MOF UTSA-16 (UTSA: University of Texas at San Antonio) has been identified as a current top-performing material in a recent review considering a range of metrics across different porous materials for carbon capture (alongside zeolite 13X and IISERP-MOF2)⁴. In particular, UTSA-16(Zn) (C₁₂H₈KO₁₄Zn₃, a zinc and citrate based MOF) has shown strong potential for industrial-scale CO₂ capture applications due to its high CO₂ adsorption (1.7 mmol/g) and selectivity (>100) at the partial pressures relevant for post-combustion capture (0.15 bar)⁸. Importantly, UTSA-16(Zn) also shows good stability to moisture and acid gases (6% and 10% decrease in capacity after exposure to 25 ppm NO₂ and SO₂ respectively)⁹, and low production costs (<1 USD/g) due to the cheap and abundant starting reagents⁹.

To translate MOFs from the lab to commercial settings, the ability to manufacture them at the required quality, scale and cost is essential. As such, principles of sustainable development and the circular economy also become important, such as minimising energy, raw materials, reagent toxicity and waste, and designing materials for reuse and recyclability¹⁰. Moving from a batch to continuous production process is therefore highly beneficial, as it offers rapid manufacture (due to high heat

and mass transfer), improved reproducibility, lower solvent and energy consumption, higher space-time yield (STY) and reactor scalability, alongside reduced downtime and labour costs (as there are fewer steps between batches)^{11,12}. Owing to these advantages, extensive research has been undertaken on the development of continuous flow syntheses for many MOFs, especially for archetypal MOFs such as HKUST-1, MIL-53, UiO-66 and ZIF-8^{13–15}.

Despite the advancements in flow chemistry for MOF production^{13,15,16}, and the benefits of UTSA-16(Zn) for CO₂ capture applications, no scalable synthesis has yet been found for this particular MOF. Herein we report the first continuous flow synthesis of MOF UTSA-16(Zn), with a very high production rate of 173 g/h and an STY of 23573 kg/m³/day. These represent a 77-fold and 15-fold increase in the production rate and STY respectively, compared to the highest previously reported for the MOF (ref: Appendix 3). This marks a significant step towards production at industrially relevant scales and subsequent application. In addition, we sought to maximise reaction sustainability, considering only low-cost, non-toxic and non-dry reagents/solvents and a low energy atmospheric pressure reactor, without the use of vacuum drying.

After synthesising the sorbent material and adsorbing CO₂, the next important step in CO₂ capture processes is separating CO₂ from the adsorbent to regenerate the material for reuse. However, the thermally insulating nature of MOFs makes thermal regeneration highly challenging, particularly at scale¹⁷. A promising approach to address this limitation is to incorporate magnetic nanoparticles (MNPs) in the MOF, forming materials known as magnetic framework composites (MFCs)^{18–20}. The inclusion of magnetic nanoparticles in the MOF enables rapid and energy-efficient regeneration by localised magnetic induction heating²¹. This process has been coined magnetic induction swing adsorption (MISA)²² and has demonstrated remarkably low energy costs associated with CO₂ capture (1.29 MJ/kg of CO₂), 45% below commercially deployed materials²³.

In this study, an in-depth optimisation of the flow synthesis for UTSA-16(Zn) is presented, considering the optimisation of chemical parameters such as reagent

ratios and concentrations, alongside an investigation into mixed-metal syntheses using magnesium, which has been reported to benefit CO₂ adsorption capacity²⁴. Physical process parameters were also investigated, including flow rate, ratios of pumps/solvents and temperature. Furthermore, citrate-coated Fe₃O₄ magnetic nanoparticles (MNP-CA) were incorporated into MOF UTSA-16(Zn) using the continuous flow method, resulting in the highest reported production rate of any MFC to-date (152 g/h), demonstrating a scalable and sustainable synthesis for the MFC UTSA-16(Zn)@MNP-CA with advantages for use in post-combustion CO₂ capture. The flow method developed herein is also applicable towards scalable manufacture of other MOFs and MFCs, aiding the broader transition of these exciting materials from the lab towards real-world applications.

2 Experimental Section

2.1 Materials

All chemicals and reagents were used as received. Zinc acetate dihydrate (≥99.0%), magnesium acetate tetrahydrate (≥99.0%), citric acid monohydrate (≥99.0%) and potassium hydroxide (86.7%) were obtained from Sigma Aldrich. Ammonium iron(III) citrate (14.5-16% Fe basis) was bought from Honeywell. Methanol (≥99.9%) was purchased from Fisher Scientific. Ethanol (absolute, SpS grade) was purchased from Scientific Laboratory Supplies LTD. All water used was deionised.

2.2 Synthesis of UTSA-16(Zn) and UTSA-16(Zn,Mg)

Synthesis of UTSA-16(Zn) was performed using a counter-current continuous flow reactor customized from perfluoroalkoxy polymer tubing (O.D: 6 mm, I.D: 4 mm) (Figure 1). Zinc acetate dihydrate (3-5 mmol), magnesium acetate tetrahydrate (0-2 mmol), citric acid monohydrate (4-6 mmol) and potassium hydroxide (12-20 mmol) were dissolved in water (10 mL) and fed *via* the downflow pump into the top of the reactor (10-80 mL/min). Water was then fed *via* the downflow pump after the reaction solution. Ethanol absolute (anti-solvent) was fed *via* the upflow pump into the bottom of the reactor (10-80 mL/min) resulting in an overall ratio of H₂O:EtOH between 2:1 and 1:2. After mixing and precipitation, the reaction stream was heated through a 14 m coil (OD: 6 mm, ID: 4 mm) in a water bath (25-85 °C, residence time:

1-9 min). A back-pressure regulator was used to prevent rapid boiling of the solvent mixtures for the reaction heated to 85 °C. The product (white solid) was then collected in suspension at the reactor outlet, centrifuged (5000 RPM) and washed with methanol (3 x 30 mL) before drying at 75 °C in an oven overnight (yield: 0.1-0.8 g, conversion yield: 9-66%, production rate: 21-341 g/h). All materials produced were consistent with the UTSA-16 structure by PXRD (without any remaining starting materials), except for the alternative crystalline phase discussed in section 3.1 (Supplementary Information, Figures S1-S9). Experimental conditions for each reaction can be found in the Supplementary Information, Tables S1-S8).

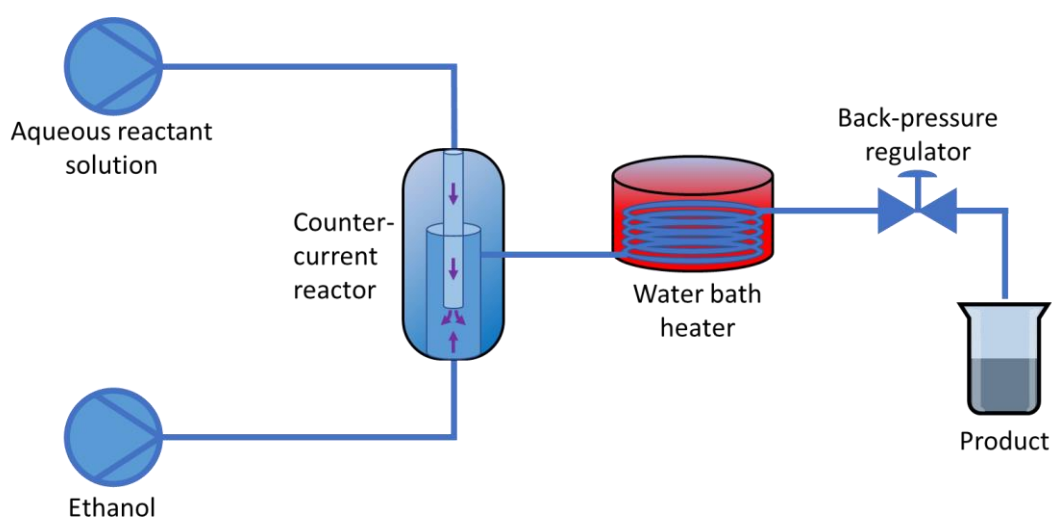


Figure 1: Schematic of the counter-current continuous flow reactor set-up used for the synthesis of UTSA-16(Zn), UTSA-16(Zn,Mg) and UTSA-16(Zn)@MNP-CA MFCs.

2.3 Extended run scale-up synthesis of UTSA-16(Zn)

The synthesis of UTSA-16(Zn) was scaled-up using the optimised procedure from section 2.2, with a larger volume of reagents (10-fold increase compared to previous optimisation runs). Zinc acetate dihydrate (0.05 mol), citric acid monohydrate (0.05 mol) and potassium hydroxide (0.15 mol) were dissolved in water (100 mL) and fed *via* the downflow pump into the top of the reactor (40 mL/min). Ethanol absolute was fed *via* the upflow pump into the bottom of the reactor (40 mL/min). The water bath heating temperature was 80 °C. After collection at the reactor outlet, the product (white solid) was centrifuged (5000 RPM) and washed with methanol (3 x 300 mL) before drying at 75 °C in an oven overnight (yield: 7.2 g, conversion yield: 59%, production rate: 173 g/h). To investigate the impact of further solvent

exchange, a portion of the product (0.8 g) was separated from the rest before drying and was subjected to additional washing and solvent exchange steps with methanol over 5 days (6 x 40 mL).

2.4 Synthesis of citrate-coated magnetite nanoparticles (MNP-CA)

Magnetic magnetite nanoparticles with a citrate coating (MNP-CA) were synthesised using a counter-current continuous hydrothermal reactor set-up, as previously reported (ref: Appendix 3). Briefly, aqueous ammonium ferric citrate (0.05 M) was fed into the bottom of the reactor at 10 mL/min. Separately, deionised water was heated to 435 °C using a 2 kW band heater and fed into the top of the reactor at 20 mL/min. The system pressure was maintained at a maximum of 24 MPa using a back-pressure regulator (Swagelok®). The reaction stream was subsequently cooled through a counter-current water heat exchanger and the product in suspension was collected at the reactor outlet. Finally, the MNP-CA was separated by gravity and magnetic attraction, washed with deionised water (3 x 25 mL) and stored in deionised water as a 5% w/v suspension.

2.5 Synthesis of UTSA-16(Zn)@MNP-CA magnetic framework composites (MFCs)

UTSA-16(Zn)@MNP-CA was synthesised based on the procedure outlined in section 2.2. Zinc acetate dihydrate (5 mmol), citric acid monohydrate (5 mmol) and potassium hydroxide (15 mmol) were first dissolved in water (8-9.5 mL). A 5% w/v solution of MNP-CA in water was then added (0.5-2 mL), bringing the total water quantity to 10 mL, and the solution fed *via* the downflow pump into the top of the reactor (40 mL/min). Water was then fed *via* the downflow pump after the reaction solution. Ethanol absolute was fed *via* the upflow pump into the bottom of the reactor (40 mL/min) resulting in an overall ratio of H₂O:EtOH of 1:1. After mixing and precipitation, the reaction stream was heated through the water bath coil (80 °C, residence time: 2 min). The product (brown solid) was then collected in suspension at the outlet, centrifuged (5000 RPM) and washed with methanol (3 x 30 mL) before drying at 75 °C in an oven overnight (yield: 0.63 g, conversion yield: 49-52%, production rate: 152 g/h).

2.6 Characterisation

Powder X-ray diffraction (PXRD). X-ray diffraction patterns of UTSA-16(Zn), MNP-CA and UTSA-16(Zn)@MNP-CA (2.9%, 11.4%) were acquired using a Bruker D8 Advance DaVinci in Bragg-Brentano geometry with a Lynxeye 1D detector and motorised air scatter screen. A Cu K α radiation source was used ($\lambda = 0.15418$ nm) at 40 kV and 40 mA. Scans were conducted between 5° and 65° 2 θ , with analyses and pattern matching performed using Bruker DIFFRAC.EVA software and powder diffraction files from the database²⁵.

Scanning electron microscopy with energy dispersive spectroscopy (SEM+EDS). High-resolution SEM images and EDS elemental analyses of UTSA-16(Zn) and UTSA-16(Zn)@MNP-CA (2.9%, 11.4%) were obtained on a Jeol 7000F FEG-SEM, using an acceleration voltage of 10-15 kV. Secondary electron images were obtained at a working distance of 10 mm with a 10 nm (approx.) carbon coating, using Jeol PC-SEM software.

Thermogravimetric analysis (TGA). TGA were carried out using a TGA550 Discovery (TA Instruments) with an automated vertical overhead thermobalance. Thermal decomposition was measured at a heating rate of 10 °C/min under an air atmosphere. CO₂ adsorption capacity was measured gravimetrically²⁶ using the following program: heat to 150 °C under N₂, hold 10 min, cool to 25 °C, switch gas to CO₂, hold 10 min. CO₂ adsorption-desorption cycling used a similar program, with an initial 150 °C activation, then a 60 °C regeneration for each desorption step. Adsorption was still performed at 25 °C.

Vibrating-sample magnetometry (VSM). Magnetometry measurements were obtained using approx. 20 mg of sample using a SQUID MPMS3 (Quantum Design). Measurements were obtained at room temperature with a field strength up to 10 kOe.

Induction heating. Induction heating measurements were undertaken using a 2 kW induction heater (204 kHz, Cheltenham Induction Heating Ltd.) according to a previously reported procedure²⁰. The temperature was measured with a fibre optic thermocouple (Neoptix Reflex) placed in a borosilicate glass tube (internal diameter:

11 mm) with 0.5 g of sample powder. The tube was positioned in a water-cooled copper coil (internal diameter: 27 mm, height: 38 mm) and a voltage was selected to supply 500 W power. All sample measurements were recorded in triplicate, plotting averages with error bars showing ± 1 standard deviation.

Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES). ICP-OES measurements were taken using an Agilent 5110 Vertical Dual View instrument with 240 place SPS-4 autosampler. Instrument operation and data processing was via the Agilent 'ICP Expert' software package. UTSA-16(Zn,Mg) samples were digested in 5% nitric acid prior to atomization in an argon plasma (5000-8000 K). Results were taken in triplicate.

3 Results and Discussion

UTSA-16(Zn), UTSA-16(Zn,Mg) and UTSA-16(Zn)@MNP-CA were synthesised using a customised pipe-in-pipe counter-current continuous flow reactor, chosen due to its simple design and rapid mixing capabilities, as described in the experimental section (Figure 1). The reactor was based on a design first reported by Lester *et al.* in 2006 to produce various nanoparicles²⁷, which has since also been used in the manufacture of archetypal MOFs such as HKUST-1, ZIF-8 and CPO-27^{28,29}. The customised reactor used in this study was made from transparent perfluoroalkoxy polymer tubing due to its high chemical resistance, also facilitating high flow rates and allowing observations during synthesis. The flow observed after mixing was laminar, with Reynolds numbers of approximately 80-322 for the 40-160 mL/min flow rates.

An initial scoping study was used to identify variables with the greatest influence on yield and CO₂ adsorption and obtain standard values from which the optimisation was based. Table 1 displays each variable, the standard values and the ranges optimised in the study. These variables were then systematically varied one-at-a-time to optimise synthesis conditions and examine the influence of each on conversion yield (%) and CO₂ adsorption (measured gravimetrically using TGA²⁶).

Table 1: Variables investigated for the synthesis optimisation study, alongside their minimum, maximum and standard values.

Variable	Min value	Max value	Standard value	Comments
Citric acid concentration (M)	0.4	0.6	0.5	Linker:base ratio kept at 1:3
KOH concentration (M)	1.30	1.95	1.5	
Mg metal mole fraction in reactants [Mg]/[Mg+Zn]	0.0	0.4	0.0	Total metal concentration [Mg+Zn] kept at 0.5 M
Solvent pump ratio [H ₂ O]/[H ₂ O+EtOH]	0.33	0.67	0.50	Total flow rate kept at 80 mL/min
Total flow rate (mL/min)	40	160	80	Ratio between pumps kept at 1:1
Water bath temperature (°C)	25	90	80	At T>80 °C a back-pressure regulator was used to prevent boiling-off
MNP-CA concentration in product (wt%)	0.0	11.4	0.0	Quantified using saturation magnetisation measurements

3.1 Optimisation of chemical parameters to maximise yield and CO₂ adsorption capacity

Initial work concentrated on the optimisation of chemical parameters to maximise the yield and CO₂ adsorption of UTSA-16(Zn). The metal concentration was fixed at 0.5 M and citric acid concentration was varied from 0.4 to 0.6 M, keeping a linker:base (L:B) ratio of 1:3. Results (Figure 2A) show that CO₂ adsorption increased from 2.1 to 3.8 mmol/g as linker concentration increased from 0.4 to 0.6 M. The yield stayed around 50% up to a linker concentration of 0.5 M after which the yield decreased from 50 to 25%. These conversion yield values are similar to others observed for MOF flow syntheses, such as 59% for MIL-53(Al)³⁰, 27% for HKUST-1¹⁶ and 24-78% for UiO-66³¹. The ratio of Zn:L:B in UTSA-16(Zn) calculated from the empirical formula (C₁₂H₈KO₁₄Zn₃)⁸ is 3:2:1. The Zn:L:B ratio used in the synthesis is typically 1:1:3^{8,9,24}, meaning that linker and base are in excess. The metal to linker ratio in MOF synthesis is typically known to have a significant effect on MOF structure and topology³². For instance, Zhou *et al.* showed that Zn-based MOFs PCN-13, PCN-131 and PCN-132 could each be produced by altering the reactants metal to linker

(anthracene-9,10-dicarboxylic acid) molar ratio between 1:1 and 5:1³³. The crystallinity of MOF-5 and the CO₂ adsorption of Cu-BTC have also been shown to depend on the metal to linker ratio^{34,35}. PXRD patterns showed that the higher linker to metal ratios resulted in a higher degree of crystallinity/crystallite size in the case of UTSA-16(Zn), with the full width at half maximum (FWHM) of the main 7.4 °2 θ peak decreasing from 0.331 to 0.201 as linker concentration increased from 0.4 to 0.6 M (Figure S2, Supplementary Information). This increase in degree of crystallinity/crystallite size (decrease in FWHM) corresponds with the CO₂ adsorption increase from 2.1 to 3.8 mmol/g. Theoretically it has been shown that if crystallite size alone is increased, the result can be a decrease in sorption capacity due to the smaller surface to volume ratio in large crystallites, as calculated with MOF Mg-MOF-74³⁶. However, if the degree of crystallinity increases, even if crystallite size also increases, this can result in an increase in sorption capacity, as observed with ZIF-8³⁷ and HKUST-1³⁸. Our result that as degree of crystallinity/crystallite size increases, so does CO₂ adsorption for UTSA-16(Zn) is therefore not unexpected.

The linker concentration was then fixed at 0.5 M (balancing the optimal yield of 50% and high CO₂ adsorption of 3.6 mmol/g), and the concentration of KOH base was varied from 1.30 to 1.95 M (Figure 2B). The yield was found to peak at 50% for a base concentration of 1.50 M before decreasing to 9% when the concentration of KOH increased from 1.50 to 1.95 M. CO₂ adsorption remained high (3.3-3.6 mmol/g) between 1.5 and 1.8 M KOH, with sharp drop-offs outside of that range to 1.4 mmol/g at 1.30 M KOH and 1.0 mmol/g at 1.95 M KOH. The effect of base concentration/pH is well documented in various MOF syntheses. It is typically considered that linker deprotonation occurs more rapidly at a high pH value, resulting in faster MOF nucleation, as observed with Zn-based MOF-5, HKUST-1 and Dy(BTC)(H₂O) MOF crystals, with an impact on sorption characteristics³⁹. PXRD patterns showed that in our case degree of crystallinity/crystallite size for UTSA-16(Zn) increased with base concentration, with the gross intensity of the 7.4 °2 θ peak increasing from 173 to 472 cps from 1.3 to 1.73 M KOH (Figure S3, Supplementary Information). This increase in degree of crystallinity/crystallite size corresponded with an increase in CO₂ adsorption from 1.4 to 3.5 mmol/g. Above 1.8 M KOH the formation of an alternative

crystalline phase was observed, with strong new peaks appearing at 9, 10 and 13 °2 θ (Figure S3, Supplementary Information). This phase could be the result of very rapid linker deprotonation at high pH, resulting in the formation of an alternative framework structure. This phenomena has also been observed for Co²⁺ with H₃BTC MOFs, where partial or full deprotonation at different pH values resulted in the formation of alternative framework structures with differing sorption characteristics⁴⁰. A value of 1.5 M for the base concentration was then taken forward, giving both optimal yield (50%) and CO₂ adsorption (3.6 mmol/g).

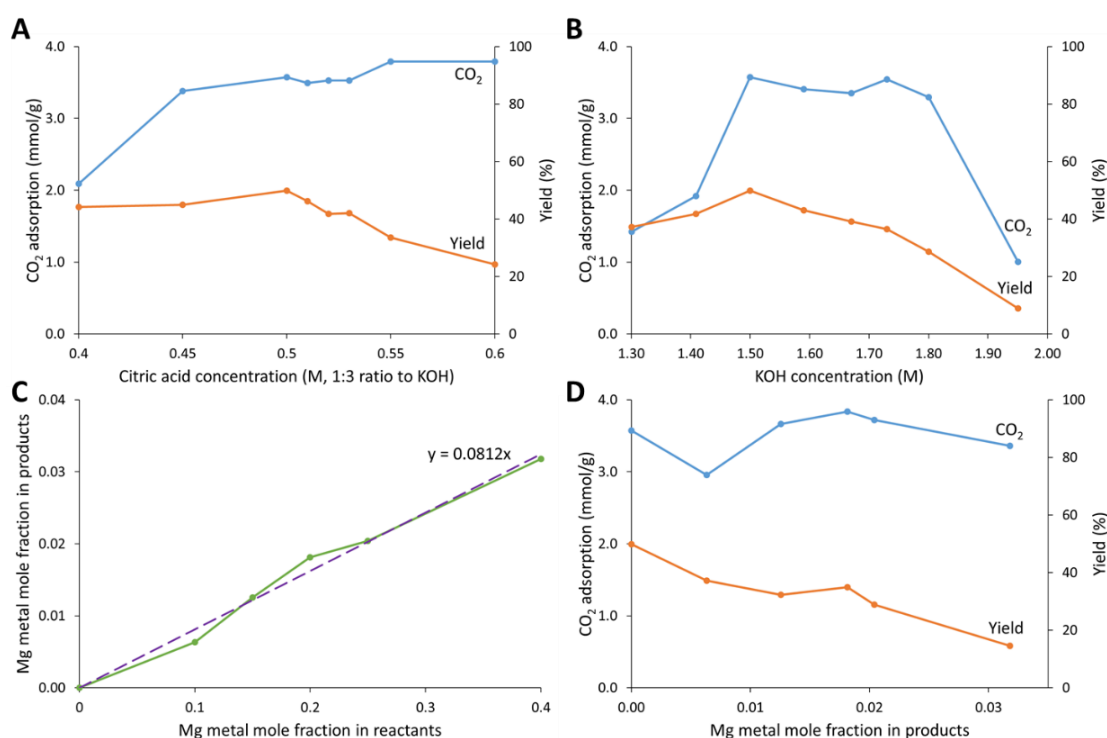


Figure 2: CO₂ adsorption capacity and yield of UTSA-16(Zn) plotted against A: citric acid concentration (with a linker:base ratio of 1:3 maintained) and B: KOH concentration. C: Mg metal mole fraction in the reactants plotted against observed Mg metal mole fraction in the products. D: CO₂ adsorption capacity and yield of UTSA-16(Zn,Mg) plotted against Mg metal mole fraction in the products.

Mixed-metal MOFs contain more than 1 type of metal ion/cluster within the nodes of their frameworks, and can be prepared by simply using a combination of metal salts during synthesis⁴¹. Often this one-pot synthesis strategy results in an approximately homogeneous dispersion of the metal ions in the MOF⁴². The combination of metals can be advantageous due to a tuning of the functionality of the MOF, including improvements to CO₂ adsorption and CO₂/N₂ selectivity⁴³. Recently Gaikwad *et al.* showed that various metals can be incorporated into UTSA-

16 via a 4 h microwave heating method²⁴. They found that synthesising UTSA-16 with a 7:2 ratio of Zn:Mg increased CO₂ capacity by 18% and CO₂/N₂ selectivity by 19% compared to pristine UTSA-16(Zn) in their method. A study to incorporate Mg into UTSA-16(Zn) via our rapid flow synthesis method was therefore conducted. ICP analysis showed that the actual concentrations of Mg incorporated in the UTSA-16(Zn,Mg) products were significantly less than those included in the reactants, approximately 8% of the expected values (*e.g.* 0.4 Mg metal mole fraction in reactants resulted in 0.032 Mg metal mole fraction in products) (Figure 2C). MOF uptake seemed to favour Zn²⁺ over Mg²⁺ over the very short timescales of our reactor (2 min residence time). Preferential incorporation of certain cations over others has also been observed in the literature for mixed-metal MOFs, and can be attributed to a number of factors including solubility, reactivity and coordination sphere⁴⁴. This effect has also been seen in the only partial incorporation of Ni into UTSA-16(Co)⁴⁵.

Figure 2D shows the impact on CO₂ adsorption and yield of the increasing Mg metal mole fraction ([Mg]/[Mg+Zn]) in the mixed-metal products. The yield was shown to decrease from 50% to 15% with increasing Mg metal mole fraction in the products from 0 to 0.032. The limited incorporation of Mg is a contributor to the decreasing yield with increasing Mg mole fraction trend. CO₂ adsorption of the materials peaked at 3.8 mmol/g at an optimal Mg mole fraction of 0.018, an increase of 0.2 mmol/g (6%) compared to pristine UTSA-16(Zn) without Mg. The differences in CO₂ adsorption after Mg inclusion into UTSA-16(Zn,Mg) could be due to changes in pore sizes, as observed with other mixed-metal Zr/Ti MOFs⁴⁶, since Mg²⁺ has a slightly smaller ionic radius (0.072 nm) compared to Zn²⁺ (0.074 nm). Changes to the open metal sites of MOFs by introducing mixed-metals has also been frequently reported to impact CO₂ adsorption capacity (due to different strengths of interactions between CO₂ and the metal cations), such as in MIL-101(Cr,Mg)⁴⁷ and the Mg-mixed CPM-200 series⁴³. However, interactions with K⁺ counterions in the pores are key to the CO₂ adsorption capacity of UTSA-16^{48,49}, so it is less likely that changes in open-metal sites are the cause of changing CO₂ capacity in this case. PXRD patterns showed an increase in degree of crystallinity/crystallite size going from no Mg to the optimal Mg mole product fraction of 0.018, with the FWHM of the 7.4 °2θ peak decreasing

from 0.222 to 0.175 (Figure SX, Supplementary Information) as CO₂ adsorption increases from 3.6 to 3.8 mmol/g. The Mg is therefore having an impact on crystallisation, and an increase in polyhedra size was observed by SEM image analysis (n=100) from 62±19 nm to 92±28 nm diameter from no Mg to the optimal Mg mole product fraction of 0.018 (Figure SX, Supplementary Information).

3.2 Optimisation of process parameters to maximise yield and CO₂ adsorption capacity

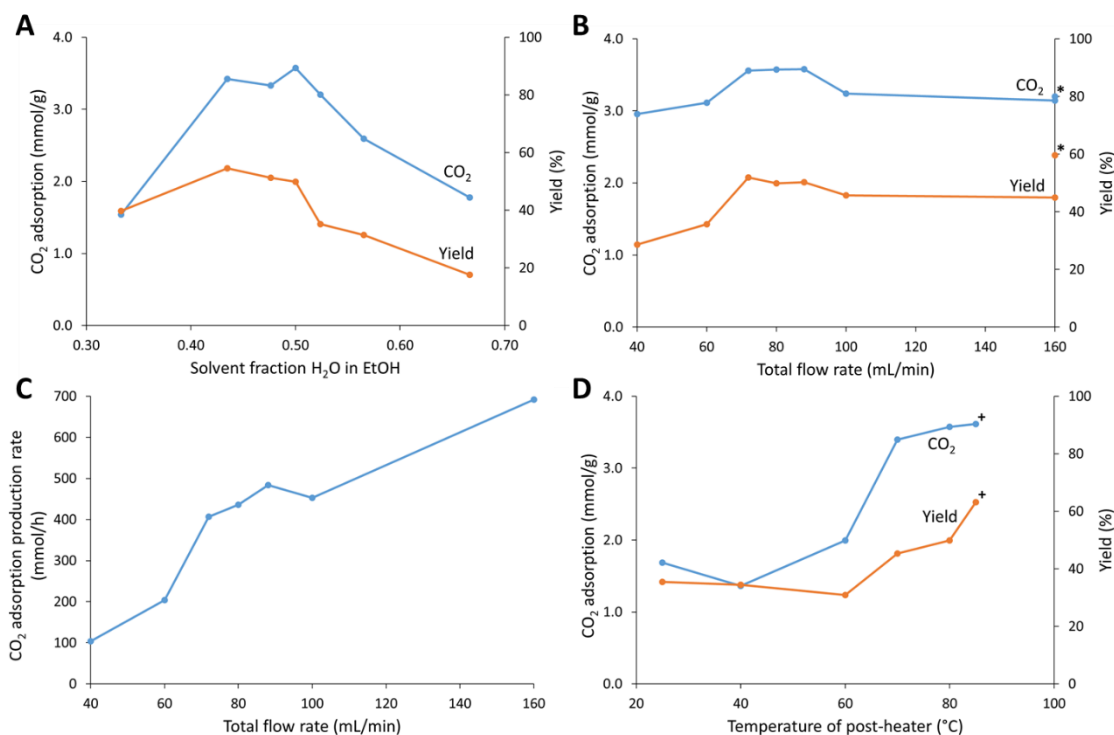
Once chemical parameters had been optimised, we then focussed on optimising the physical processing variables. As described in the experimental section, our flow rig (Figure 1) included an aqueous reactant solution pump and an ethanol solvent pump. The ratio of these two pumps (ensuring the total flow rate was kept constant) was varied from 1:2 H₂O:EtOH (0.33 solvent fraction H₂O) to 2:1 H₂O:EtOH (0.67 solvent fraction H₂O). The associated impact on CO₂ adsorption and yield are shown in Figure 3A. A ratio of 1:1 was found to be optimal for CO₂ adsorption (3.6 mmol/g), though yield could be increased from 50% to 55% by increasing the EtOH antisolvent ratio from H₂O:EtOH 1:1 to 1:1.3. This increase in EtOH ratio did however result in a decrease to 3.4 mmol/g CO₂ adsorption. PXRD patterns showed that at high H₂O ratios the degree of crystallinity/crystallite size for UTSA-16(Zn) was reduced, with the FWHM of the 7.4 °2θ peak increasing from 0.222 to 0.292 from H₂O:EtOH 1:1 to 2:1. This reduction corresponded with the observed decrease in CO₂ adsorption from 3.6 to 1.8 mmol/g, as discussed previously in section 3.1. At high EtOH ratios, the beginnings of an alternative crystal structure were observed (Figure S5, Supplementary Information). This alternative structure was the same as that observed at high pH described earlier in section 3.1 (Figure S3, Supplementary Information). This supports our earlier suggestion that the alternative structure results from the MOF nucleating too quickly to form the usual phase, as high EtOH antisolvent ratios would also result in very rapid nucleation. A similar rate of formation effect is seen in the modulated synthesis of MOFs, where the addition of a modulator can slow down the self-assembly process changing the phase or topology produced⁵⁰. An example is the use of benzoic acid as a modulator to influence the kinetics of the self-assembly of MIL-101(Cr), resulting in the alternative

formation of MIL-88B(Cr)⁵¹. The SEM micrographs showed formation of rod-like crystals in the 1:2 H₂O:EtOH sample containing the alternative PXRD structure, attributed to the new phase, which were not visible in the samples at other solvent ratios (Figure S11, Supplementary Information). In addition to rate of formation, solvents are also known to play a significant role in the synthesis and morphology determination of MOFs. An example is the various crystal structures of Mg PDC MOFs produced by different solvents under the same reaction conditions⁵². The H₂O:EtOH solvent ratio has also been shown to affect the crystallisation process of Mg BTC MOFs⁵³, where the ratios produced different structures as the result of a complex and sensitive process based on solubility properties and coordination behaviour of the metal cations in the different solvent ratios.

Keeping the aqueous and ethanol pumps at a 1:1 ratio, the total flow rate was varied between 40 and 160 mL/min (Figure 3B). The yield increased steeply from 29% to 50% as flow rate increased from 40 mL/min to 80 mL/min, before gradually decreasing to 45% as flow rate increased further to 160 mL/min. This trend likely represents the combination of two overlapping factors, dominant in different flow-rate ranges. The factors are reactor mixing intensity (increases with flow rate⁵⁴, dominant impact at lower flow rates <80 mL/min) and heating coil residence time (decreases with flow rate, dominant at higher flow rates >80 mL/min), both influenced by flow rate⁵⁵. These impacts were confirmed through separating the factors of mixing intensity and residence time. A sample was pumped through the mixing reactor at 160 mL/min, before the pumps were decreased to a total flow rate of 20 mL/min as the sample passed through the heater coil (maximising both mixing intensity and residence time). This sample is marked with a * in Figure 3B. The yield for this sample was higher than the run kept at 160 mL/min throughout, confirming that the higher residence time resulted in a higher yield for a set mixing reactor flow rate. As with other flow chemistry processes, longer reaction/residence times typically result in a greater conversion/extent of reaction, resulting in an increased product yield⁵⁶. CO₂ adsorption also increased from 3.0 to 3.6 mmol/g as flow rate increased from 40 mL/min to 80 mL/min, before gradually decreasing to 3.1 mmol/g as flow rate increased further to 160 mL/min. However, the CO₂ adsorption of the *

sample (Figure 3B, 160-20 mL/min) was no higher than that of the run kept at 160 mL/min throughout. A minimum timescale is likely still required for thermodynamically favourable products to be reached, as too short reaction times can result in the formation of kinetically favoured products^{57,58}. However, across our range of flow rates (40-160 mL/min), longer residence time was not beneficial for CO₂ adsorption, and mixing intensity was the dominant factor. It is therefore proposed that mass transfer/mixing efficiency was optimised around 80 mL/min for our rig, and greater flow rates/intensity don't result in more efficient mixing⁵⁹. An optimal mixing intensity is therefore crucial for optimising the synthesis of UTSA-16(Zn) and must be carefully considered if transferring the synthesis to an alternative flow-rig or scaling up the reactor size⁶⁰.

PXRD patterns of different flow rate samples again showed the link between CO₂ adsorption and degree of crystallinity/crystallite size, with the FWHM of the 7.4 °2 θ peak decreasing from 0.316 to 0.222 from 40 to 80 mL/min (3.0 to 3.6 mmol/g CO₂ adsorption), then increasing from 0.222 to 0.350 from 80 to 160 mL/min (3.6 to 3.1 mmol/g CO₂ adsorption) (Figure S6, Supplementary Information). SEM image analysis showed no significant differences in crystal size or morphology between the different flow rates (Figure S11, Supplementary Information). Figure 3C shows the CO₂ adsorption capacity production rate in mmol/h, calculated by combining the different CO₂ adsorption capacities, yields and reaction times for the individual flow rates. The results showed an approximately linear trend of CO₂ adsorption production rate increasing from 104 to 692 mmol/h from 40 to 160 mL/min. A peak increase in CO₂ adsorption production rate from the trend was observed between 72 and 88 mL/min due to the enhanced product quality in this range, with CO₂ adsorption at 3.6 mmol/g compared to 3.0-3.2 mmol/g at the lower (≤ 60 mL/min) and higher (≥ 100 mL/min) flow rates. The implication of these results is that despite CO₂ adsorption and % yield decreasing at the higher flow rates (≥ 100 mL/min, Figure 3B), the CO₂ adsorption production rate still increases with flow rate up to at least 160 mL/min, facilitating greater scale-up possibilities. CO₂ adsorption production rate is not typically calculated in the literature for comparison, though mass production rate is frequently compared as discussed below in section 3.3.



*Mixing in reactor at 160 mL/min, decrease to 20 mL/min through heater coil, return to 160 mL/min for collection.

[†]Back-pressure regulator was used to prevent rapid solvent boiling.

Figure 3: CO₂ adsorption capacity and product yield of UTSA-16(Zn) plotted against A: solvent fraction H₂O in EtOH, B: total flow rate. C: CO₂ adsorption capacity production rate of UTSA-16(Zn) plotted against flow rate. D: CO₂ adsorption capacity and product yield of UTSA-16(Zn) plotted against temperature of the water bath post-heater.

Temperature is another important factor effecting MOF synthesis. Our flow rig design included a water bath coil heater which the MOF suspension was fed through after mixing with the antisolvent in the counter-current reactor. The temperature of the bath was varied between 25 and 85 °C, and the impact on the CO₂ adsorption and yield of the product were measured (Figure 3D). No significant changes were observed in either metric from 25 to 60 °C. However, between 60 and 85 °C there was a steep increase in CO₂ adsorption from 2.0 to 3.6 mmol/g, and yield from 31% to 66% with increasing temperature. At 85 °C, a back-pressure regulator was employed to prevent rapid solvent boiling. Thermodynamically, the formation of MOFs can be either endothermic or exothermic^{61,62}. Irrespectively, higher temperatures result in a higher kinetic energy of the reactants, enabling them to overcome the activation energy and resulting in shorter reaction times, as observed with MOF-5⁶³. Reactions at higher temperatures tend to lead to denser structures with higher degrees of framework connectivity and lower levels of solvation⁵⁸, and

also support the formation of more thermodynamically favoured structures, as demonstrated with various Zn and Cu-based MOFs^{64,65}. Higher degrees of crystallinity are typically thermodynamically favoured⁶⁶, resulting in more crystalline materials at higher reaction temperatures. This is supported by a study on the mixed-metal MOF UTSA-16(Co,Zn), where lower temperature (≤ 60 °C) produced primarily amorphous products, with improved crystallinity at temperatures ≥ 80 °C⁸. The same result was observed here in the case of UTSA-16(Zn) by PXRD analysis (Figure S7, Supplementary Information). The patterns evidenced the dependence of the degree of crystallinity/crystallite size of UTSA-16(Zn) on temperature, with the FWHM of the $7.4^\circ 2\theta$ peak decreasing from 0.357 at 25 °C to 0.214 at 85 °C, corresponding with the CO₂ adsorption increasing from 1.7 to 3.6 mmol/g. The higher temperatures enable sufficient energy for reorganisation of the initially disordered MOF structure, leading to the more thermodynamically stable and ordered crystalline structure. A similar transition has been reported with MOF UiO-66-NH₂, where a two-step procedure with heating led to reorganisation of the framework structure to increase crystallinity⁶⁷.

3.3 Impact of scaling-up synthesis on yield and CO₂ adsorption

The optimisation of the chemical and physical parameters were conducted using run sizes of approximately 1 g scale. Considering just the time of the reactants through the counter-current reactor (i.e. treating the individual run as part of a continuous run, not including set-up or collection times), each reaction ran for 15 seconds. To test the initial scope for scale-up, the reactor was run for 10x the duration, 2.5 minutes, approximately 10 g scale. Figure 4A shows the impact of this scale-up trial on the CO₂ adsorption and yield of the UTSA-16(Zn). The CO₂ adsorption was approximately the same (3.6 mmol/g) on the 1 g and 10 g scales, as expected, but the yield showed a significant increase from 50% to 59% from 1 g to 10 g scale. This was most likely due to reduced losses in product collection when scaling up (less proportion of material left in the tubing). PXRD patterns showed no significant differences in the degree of crystallinity/crystallite size upon moving from 1 g to 10 g scale, with the FWHM of the $7.4^\circ 2\theta$ peak shifting from 0.222 to 0.218 (Figure S8, Supplementary Information). SEM analyses revealed a similar morphology for 1 g and

10 g scale, revealing mostly 50-100 nm polyhedra (Figure S12, Supplementary Information). These results demonstrate the reliability and consistency of the flow process in producing UTSA-16(Zn). For UTSA-16(Zn) (10x scale), the recyclability of the MOF was measured over 12 cycles of CO₂ adsorption-desorption (Figure 4B). Previous results in this study have used a 150 °C activation temperature prior to measuring CO₂ adsorption. However, in order to test CO₂ desorption efficiency at lower regeneration temperatures (reducing energy usage), 60 °C was selected for CO₂ desorption during the cycling. The lower regeneration temperature resulted in a slight decrease in CO₂ adsorption (3.6 mmol/g for 150 °C regeneration, 3.3 mmol/g for 60 °C regeneration), as previously observed (ref: Appendix 3). However, no decrease in the CO₂ adsorption capacity over the 12 cycles was observed (cycle 1: 3.23 mmol/g, cycle 12: 3.29 mmol/g). This contrasts with the decreasing capacity observed for some other materials such as an amine-based adsorbent (7% decrease over 19 cycles)⁶⁸ and zeolite Y templated carbon (6% decrease over 5 cycles)⁶⁹, due to incomplete regeneration between cycles.

Key performance metrics for scale-up are production rate (g/h) and space time yield (STY, kg/m³/day)⁷⁰. Our 10 g scale synthesis demonstrated a production rate of 173 g/h and an STY of 23,573 kg/m³/day, treating the individual run as part of a continuous run and using the heating coil as the reactor volume⁵⁵. This represents a 77-fold increase in production yield and a 15-fold increase in STY for UTSA-16(Zn) compared to the previous records (microwave batch process: production rate: 2.25 g/h, STY: 1543 kg/m³/day) (ref: Appendix 3), demonstrating the benefits of a continuous flow synthesis. Production rate is considered a more representative metric for comparing MOF flow syntheses, as STYs are prone to over-extrapolation and have high variation based on how the reactor or reaction mixture volume is calculated^{55,70}. Typical STY values for MOF flow syntheses are between 400 and 10,000 kg/m³/day^{15,70}, though values as high as 6.32×10^5 have been reported⁷¹. Successful scale-up of production rate using flow-syntheses of other MOFs has been observed from a variety of reactor designs, including HKUST-1 (60 g/h)¹⁴, MIL-53(Al) (125 g/h)³⁰, UiO-66 (104 g/h)⁷², CPO-27(Ni) (132 g/h)²⁹, and ZIF-8 (27 g/h lab scale, 810 g/h pilot scale reactor)²⁸. Based on similar reactor designs to ours at a larger

scale, transfer from our lab-scale flow reactor to a larger pilot-scale reactor would also be possible for further scale-up of production rate²⁸.

As described in the experimental section, our standard collection and washing/activation protocol involved consolidation by centrifuge, washing three times with methanol and drying in an oven overnight. In order to see if further MOF activation would be possible, a small aliquot of the 10 g scale run (0.8 g) was separated before drying and subject to a further 6 methanol washing steps with solvent exchange over 5 days. The extra washing steps resulted in an increase from 3.6 to 3.8 mmol/g CO₂ adsorption (Figure 4). This increase shows that the UTSA-16(Zn) is not fully activated from the standard protocol, and further improvements to the CO₂ adsorption capacity could be made through optimisation of the washing and activation procedure. However, if additional solvent, time and energy (e.g. vacuum drying or drying solvents) are required for these improvements, as have been used previously for UTSA-16(Zn)^{8,9}, due consideration should be given to the negative impacts on the sustainability and scalability of the manufacturing process¹⁰. For instance, in our extra washing case, a 6% increase in CO₂ adsorption cost a 267% increase in washing solvent quantity and an additional 5 days (compared to 0 days) of solvent soaking time. PXRD and SEM analyses showed that the extra washing steps caused no differences in the previously described crystallinity or morphology of the MOF (Figures S8, S12, Supplementary Information). The increase in CO₂ adsorption is therefore attributed to the further removal of water/solvent molecules from the MOF pores⁷³.

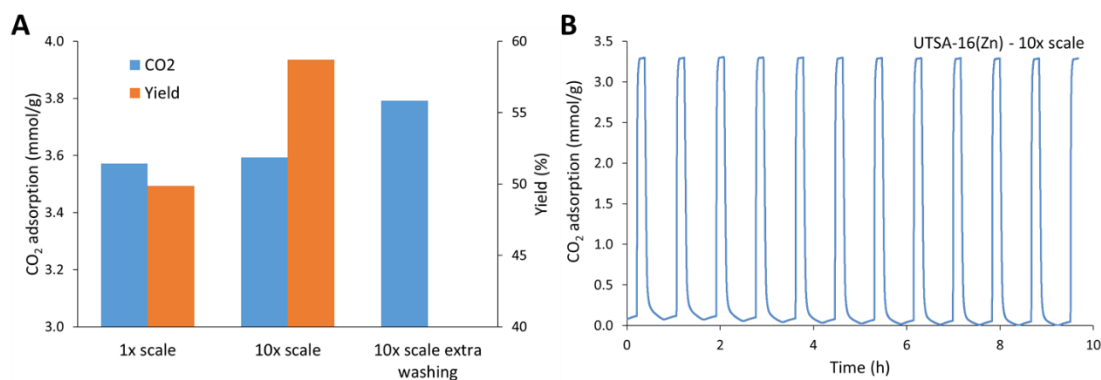


Figure 4: A: CO₂ adsorption capacity and product yield of UTSA-16(Zn) produced at 1x scale and 10x scale, and CO₂ adsorption measured after additional washing steps on a sample of the 10x scale run. B: CO₂ adsorption capacity for UTSA-16(Zn) (10x scale) over 12 adsorption-desorption cycles. Regeneration was performed at 60 °C.

3.4 Incorporation of Fe₃O₄ into UTSA-16(Zn)

As discussed in the introduction, incorporation of magnetic nanoparticles into MOFs, forming MFCs, enables rapid and energy efficient induction heating to be used for material regeneration for reuse. Herein, we successfully synthesised MFCs at a production rate of 152 g/h using the continuous flow method developed for UTSA-16(Zn) (Figure 1). This production rate is the highest reported for any MFC to-date (previous highest of 13 g/h for MgFe₂O₄@UiO-66-NH₂)⁷⁴. The MFCs contained 2.9 and 11.4 wt.% MNP-CA, quantified through saturation magnetisation measurements²³ (Figure 5A). These values are similar to those previously reported in our group using a microwave batch method (ref: Appendix 3) and other reported MFCs from the literature, such as 0.1-7.8 wt% Fe₃O₄ in Mg-MOF-74⁷⁵, 2.0-4.1 wt% MgFe₂O₄ in UiO-66²² and 1.3-7.3 wt% Fe₃O₄ in PCN-250⁷⁶.

Figure 5B shows the impact on CO₂ adsorption and yield after incorporating the MNP-CA into UTSA-16(Zn). The product yield was shown to be unaffected by composite formation, remaining around 50%. This value is higher than observed elsewhere for the flow synthesis of an MFC, such as 18-34% for MgFe₂O₄@UiO-66-NH₂⁷⁴. The absolute CO₂ adsorption was shown to decrease with increasing MNP-CA content, from 3.6 to 3.1 mmol/g from 0 to 11.4 wt.% MNP-CA. This decrease was expected due to MNP-CA not adsorbing CO₂. However, once the mass of MNP-CA in the MFCs was accounted for, there was no decrease observed in the CO₂ capacity of the MOF, remaining around 3.6 mmol/g. This demonstrates that the MNP-CA incorporation had no detrimental impact on the MOF's synthesis or CO₂ capacity, which could have

occurred or been expected due to pore blocking effects^{77,78}. The recyclability of UTSA-16(Zn)@MNP-CA (11.4%) was measured over 12 cycles of CO₂ adsorption-desorption (Figure 5D), as performed on the pure MOF in section 3.3 and Figure 4B. Once again, a low regeneration temperature of 60 °C was used for the CO₂ desorption steps, and resulted in a slight decrease in capacity compared to the higher 150 °C desorption (3.1 mmol/g for 150 °C, 2.9 mmol/g for 60 °C). Similarly to that observed for pristine UTSA-16(Zn) in section 3.3, there was no decrease in the CO₂ adsorption capacity over the 12 cycles (cycle 1: 2.89 mmol/g, cycle 12: 2.89 mmol/g). In addition, UTSA16(Zn)@MNP-CA MFCs were all found to be thermally stable up to 250 °C, the same as the pristine MOF, demonstrating that MNP-CA incorporation had no detrimental impact on the thermal stability of UTSA-16(Zn) (Figure S10, Supplementary Information).

Overall, the CO₂ capacities obtained for UTSA-16(Zn) and the UTSA16(Zn)@MNP-CA MFCs were comparable to those previously reported for pristine UTSA-16(Zn) (3.5 mmol/g solvothermal batch⁸, 3.4 mmol/g microwave batch (ref: Appendix 3) and other high performing MOFs/MOF composites^{79,80}, though were not as high as the absolute maximum reported value for pristine UTSA-16(Zn) (4.7 mmol/g)⁹. The added advantages in this case are the low-cost and scalable flow synthesis route, short washing and activation procedure, high production rate, and capability for magnetic induction heating for localised low-energy regeneration. PXRD measurements confirmed the presence and crystallinity of both the MOF and MNP-CA components in the UTSA16(Zn)@MNP-CA MFCs, with Fe₃O₄ peaks at 30, 36 and 43 °2 θ representing the MNP-CA (ref: Appendix 3) (Figure S9, Supplementary Information). The distribution of the MNP-CA in the UTSA-16(Zn) was probed by SEM with EDS elemental analysis (Figure S13, Supplementary Information). MNP-CA (Fe, red) was shown to be well dispersed in the UTSA-16(Zn) (Zn, green) structure. The reasonably uniform distributions of MNP-CA throughout the MFCs meant a high wt.% MOF loading (89-97%) could be used, maximising gravimetric CO₂ adsorption capacity, while still allowing effective induction heating throughout the material. These MFC structures are distinct from others frequently observed in the literature, for instance thin MOF layers grown on individual nanoparticles such as HKUST-1 on Fe₃O₄^{81,82} or

ZIF-8 on Fe_3O_4 ⁸³. These core-shell structures typically have much lower wt.% MOF loadings in the composites^{81,82} and are prepared by many-step layer-by-layer syntheses. The UTSA-16(Zn)@MNP-CA structure is also distinct from MFCs grown via slow direct-growth methods, where large MOF crystals grow around nanoparticles. Examples of these structures include MgFe_2O_4 in Mg-MOF-74²³ or Fe_3O_4 in Co-MOF-74⁸⁴, formulated over 15 h and 2.5 day syntheses, respectively.

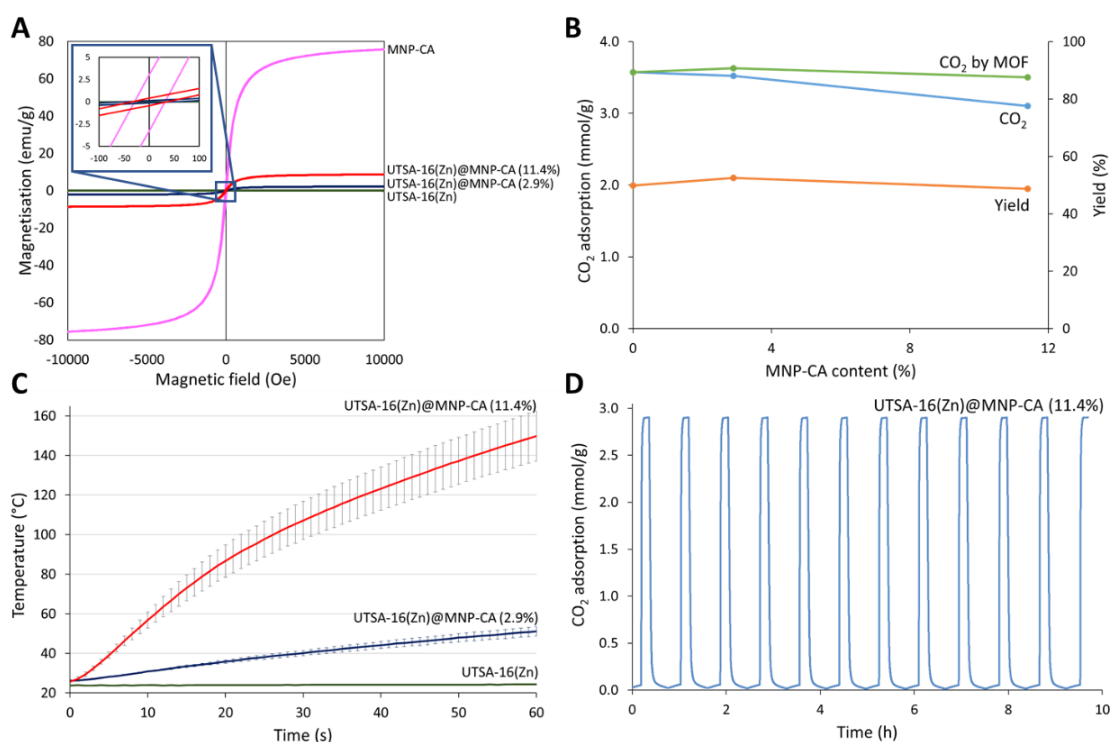


Figure 5: A: VSM measurements of UTSA-16(Zn), UTSA 16(Zn)@MNP-CA MFCs, and MNP-CA taken at room temperature with a field strength up to 10 kOe. B: CO₂ adsorption capacity and product yield of UTSA-16(Zn)@MNP-CA plotted against MNP-CA content. C: Temperature reached by induction heating plotted against time for UTSA-16(Zn) and UTSA 16(Zn)@MNP-CA MFCs at 500 W over 30 s. Results are an average over 3 runs with error bars showing ± 1 standard deviation. D: CO₂ adsorption capacity for UTSA-16(Zn)@MNP-CA (11.4%) over 12 adsorption-desorption cycles. Regeneration was performed at 60 °C.

The saturation magnetisation values of the MFCs were measured by VSM analysis to be 2.2 and 8.6 emu/g for UTSA-16(Zn)@MNP-CA (2.9%) and UTSA-16(Zn)@MNP-CA (11.4%) respectively (Figure 5A). Similar values have been reported for other MFCs in the literature, showing a range of values from 1.5-4 emu/g for MgFe_2O_4 in UiO66²², 0.1-3.9 emu/g for Fe_3O_4 in Mg-MOF-74⁷⁵ and 3.1-18.4 emu/g for Fe_3O_4 in PCN-250⁷⁶. For comparison, pristine UTSA-16(Zn) and MNP-CA had saturation magnetisations of 0.0 and 75.7 emu/g, respectively. Induction heating tests were conducted for the pristine MOF and MFCs at 500 W over a 60 s period (magnetic field: 164 A/m), with

the results shown in Figure 5C. As anticipated, pristine UTSA-16(Zn) showed no heating over the time period, and the higher MNP-CA concentration in the MFC resulted in a much faster heating rate than the lower concentration (26-150 °C over 60 s for UTSA-16(Zn)@MNP-CA (11.4%) and 26-51 °C over 60 s for UTSA-16(Zn)@MNP-CA (2.9%)). A balance between CO₂ capacity and induction heating rate can be achieved when considering the optimal concentration of MNP-CA in the MFC, which may vary depending on the application environment. As shown in Figure 5D, temperatures as low as 60 °C can result in effective desorption in repeated adsorption-desorption cycling without loss of capacity for UTSA-16(Zn)@MNP-CA. This is much lower than temperatures typically required for other adsorbents such as zeolites (200 °C)⁸⁵, carbon-based materials (120-230 °C)⁸⁶, and other MFCs (130-145 °C)²³. Furthermore, due to the efficiency of the magnetic induction heating method, temperatures required for the desorption step can be reached in seconds (e.g. 60 °C in 11 s for UTSA-16(Zn)@MNP-CA (11.4%), Figure 5C). Typical regeneration times have been shown to range between 20-40 min for alternative adsorbents such as activated carbon and zeolites using conventional or microwave heating^{87,88}, and previous MFCs have demonstrated regeneration times as fast as 4-11 min via magnetic induction heating^{22,23,89}.

4 Conclusions

Herein we report the first continuous flow synthesis of promising CO₂ capture MOF UTSA-16(Zn). A high production rate (173 g/h) and STY (23573 kg/m³/day) were achieved compared to batch synthesis (2.25 g/h, 1543 kg/m³/day), representing a 77-fold and 15-fold increase respectively. The lab-scale reactor design has been shown to be scalable, and higher flow rates resulted in higher CO₂ adsorption capacity production rates (692 mmol/h at 160 mL/min). The described procedure marks a significant step towards industrial application for UTSA-16(Zn), maximising reaction sustainability through low-cost and non-toxic reagents and a low-energy atmospheric pressure flow reactor.

A detailed optimisation study identified key variables and their impacts on the MOF's CO₂ adsorption and product yield metrics. The optimal Zn:L:B reagent ratio was found to be 1:1:3 (3.6 mmol/g, 50% yield), with further increases to the L and B concentrations improving the CO₂ capacity at the expense of the yield (3.8 mmol/g, 24% yield at 1:1.2:3.6 Zn:L:B). CO₂ adsorption was also found to increase with an optimum concentration of incorporated Mg (3.8 mmol/g at 0.018 Mg metal mole fraction in product), though only approx. 8% of the added Mg was incorporated, with associated losses to the overall yield (35%).

Both CO₂ adsorption and yield were found to be very sensitive to the H₂O:EtOH solvent ratio, with a 1:1 ratio giving the best results (3.6 mmol/g, 50% yield). The optimal reactor mixing efficiency to maximise CO₂ adsorption was found to be at an 80 mL/min flow rate (3.6 mmol/g), and the yield could be further improved (up to 60%) using a lower flow rate (20 mL/min, longer residence time) through the coil heater. Both CO₂ adsorption and yield were found to improve with higher heating temperatures (from 1.7 mmol/g, 35% yield at 25 °C up to 3.6 mmol/g, 63% yield at 85 °C), though a back-pressure regulator was required above 80 °C to prevent solvent boiling. A 10-fold increase in run size through extending the run-time of the reactor (15 s for 1 g scale, 2.5 min for 10 g scale) was found to benefit the yield (59% at 10 g scale compared to 50% at 1 g scale) and maintained a high CO₂ adsorption (3.6 mmol/g). Additional washing tests showed that further increases to CO₂ capacity were possible (3.8 mmol/g) though extra washing and solvent soaking steps, at the expense of the reaction sustainability.

Finally, citrate-coated Fe₃O₄ magnetic nanoparticles were added into the flow synthesis of UTSA-16(Zn), producing MFCs with 2.9 and 11.4 wt.% incorporated MNP-CA. No detrimental effects were observed on the yield (≈50%), CO₂ adsorption capacity of the MOF component (≈3.6 mmol/g), or recyclability (no loss in capacity over 12 cycles). Saturation magnetisations of 2.2 and 8.6 emu/g were measured for UTSA-16(Zn)@MNP-CA (2.9%) and UTSA-16(Zn)@MNP-CA (11.4%) respectively. The MFCs demonstrated rapid heating under a magnetic field (26-150 °C over 60 s for UTSA-16(Zn)@MNP-CA (11.4%)), highly beneficial for material regeneration for

reuse. This represents the largest production rate of any reported MFC to date (152 g/h) and demonstrates the scalability of this novel class of materials.

The flow method developed herein will facilitate the transfer of UTSA-16(Zn) and UTSA-16(Zn)@MNP-CA syntheses to pilot-scale reactors, enabling the larger-scale testing of the materials in CO₂ capture application environments. The methods developed will also aid in the discovery and understanding of other MOFs/MFCs, supporting their transition to larger scale manufacture and broad industrial applications.

5 Author contributions

John Luke Woodliffe: Conceptualization, Formal Analysis, Validation, Investigation, Methodology, Writing – Original Draft, Writing – Review & Editing, Visualization. Oday Hussein: Investigation (vibrating sample magnetometry). Ed Lester: Resources, Writing – Review & Editing. Rebecca Ferrari: Writing – Review & Editing. Ifty Ahmed: Conceptualization, Supervision, Writing – Review & Editing. Andrea Laybourn: Conceptualization, Project Administration, Supervision, Writing – Review & Editing, Funding Acquisition (EPSRC CDT).

6 Conflicts of interest

There are no conflicts to declare.

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Supplementary Information

Continuous flow synthesis of MOF UTSA-16(Zn), mixed-metal and magnetic composites for CO₂ capture – toward sustainable and scalable manufacture

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Experimental conditions

Citric acid concentration study (1:3 ratio to KOH)

Table S1: experimental conditions for the citric acid concentration study, with a 1:3 ratio of citric acid to KOH.

Sample	Temp. (°C)	Flow rate (mL/min)	Ratio H ₂ O:EtOH	Conc. (M) ZnOAc ₂	Conc. (M) citric acid	Conc. (M) KOH
1	80	80	1:1	0.5	0.4	1.2
2	80	80	1:1	0.5	0.45	1.35
3	80	80	1:1	0.5	0.5	1.5
4	80	80	1:1	0.5	0.51	1.53
5	80	80	1:1	0.5	0.52	1.56
6	80	80	1:1	0.5	0.53	1.59
7	80	80	1:1	0.5	0.55	1.65
8	80	80	1:1	0.5	0.6	1.8

KOH concentration study

Table S2: experimental conditions for the KOH concentration study.

Sample	Temp. (°C)	Flow rate (mL/min)	Ratio H ₂ O:EtOH	Conc. (M) ZnOAc ₂	Conc. (M) citric acid	Conc. (M) KOH
9	80	80	1:1	0.5	0.5	1.30
10	80	80	1:1	0.5	0.5	1.41
11	80	80	1:1	0.5	0.5	1.50
12	80	80	1:1	0.5	0.5	1.59
13	80	80	1:1	0.5	0.5	1.67
14	80	80	1:1	0.5	0.5	1.73
15	80	80	1:1	0.5	0.5	1.8
16	80	80	1:1	0.5	0.5	1.95

Zn/Mg mixed-metal study

Table S3: experimental conditions for the Zn/Mg mixed-metal study.

Sample	Temp. (°C)	Flow rate (mL/min)	Ratio H ₂ O:EtOH	Conc. (M) ZnOAc ₂	Conc. (M) MgOAc ₂	Conc. (M) citric acid	Conc. (M) KOH
17	80	80	1:1	0.5	0	0.5	1.5
18	80	80	1:1	0.45	0.05	0.5	1.5
19	80	80	1:1	0.425	0.075	0.5	1.5
20	80	80	1:1	0.4	0.1	0.5	1.5
21	80	80	1:1	0.375	0.125	0.5	1.5
22	80	80	1:1	0.3	0.2	0.5	1.5

Solvent ratio H₂O:EtOH study

Table S4: experimental conditions for the H₂O:EtOH solvent ratio study

.Sample	Temp. (°C)	Flow rate (mL/min)	Ratio H ₂ O:EtOH	Conc. (M) ZnOAc ₂	Conc. (M) citric acid	Conc. (M) KOH
23	80	80	2:1	0.5	0.5	1.5
24	80	80	1.3:1	0.5	0.5	1.5
25	80	80	1.1:1	0.5	0.5	1.5
26	80	80	1:1	0.5	0.5	1.5
27	80	80	1:1.1	0.5	0.5	1.5
28	80	80	1:1.3	0.5	0.5	1.5
29	80	80	1:2	0.5	0.5	1.5

Total pumps flow rate study

Table S5: experimental conditions for the pumps flow rate study

Sample	Temp. (°C)	Flow rate (mL/min)	Ratio H ₂ O:EtOH	Conc. (M) ZnOAc ₂	Conc. (M) citric acid	Conc. (M) KOH
30	80	40	1:1	0.5	0.5	1.5
31	80	60	1:1	0.5	0.5	1.5
32	80	72	1:1	0.5	0.5	1.5
33	80	80	1:1	0.5	0.5	1.5
34	80	88	1:1	0.5	0.5	1.5
35	80	100	1:1	0.5	0.5	1.5
36	80	160	1:1	0.5	0.5	1.5
37	80	160 – 20	1:1	0.5	0.5	1.5

Water bath temperature study

Table S6: experimental conditions for the water bath temperature study

Sample	Temp. (°C)	Flow rate (mL/min)	Ratio H ₂ O:EtOH	Conc. (M) ZnOAc ₂	Conc. (M) citric acid	Conc. (M) KOH
38	25	80	1:1	0.5	0.5	1.5
39	40	80	1:1	0.5	0.5	1.5
40	60	80	1:1	0.5	0.5	1.5
41	70	80	1:1	0.5	0.5	1.5
42	80	80	1:1	0.5	0.5	1.5
43	85	80	1:1	0.5	0.5	1.5

Scale-up and extra washing study

Table S7: experimental conditions for the scale-up and extra washing study

Sample	Temp. (°C)	Flow rate (mL/min)	Ratio H ₂ O:EtOH	Conc. (M) ZnOAc ₂	Conc. (M) citric acid	Conc. (M) KOH	Scale	Extra washing
44	80	80	1:1	0.5	0.5	1.5	1 g	X
45	80	80	1:1	0.5	0.5	1.5	10 g	X
46	80	80	1:1	0.5	0.5	1.5	1 g	✓

Incorporation of citrate-coated Fe₃O₄ nanoparticles (MNP-CA) study

Table S8: experimental conditions for the incorporation of citrate-coated Fe₃O₄ nanoparticles study

Sample	Temp. (°C)	Flow rate (mL/min)	Ratio H ₂ O:EtOH	Conc. (M) ZnOAc ₂	Conc. (M) citric acid	Conc. (M) KOH	Vol. 5 wt.% MNP-CA sol ⁿ added (mL)
47	80	80	1:1	0.5	0.5	1.5	0
48	80	80	1:1	0.5	0.5	1.5	0.5
49	80	80	1:1	0.5	0.5	1.5	2

PXRD patterns of UTSA-16(Zn) and analogues

UTSA-16(Zn) compared to zinc acetate and citric acid

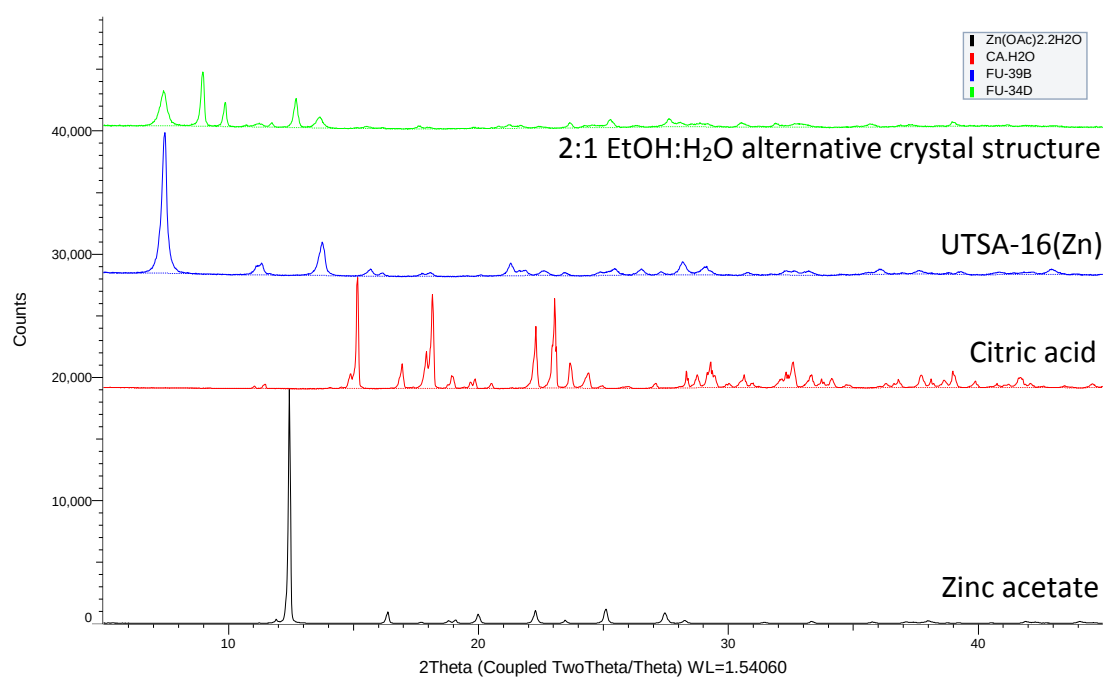


Figure S1: PXRD patterns of zinc acetate, citric acid and UTSA-16(Zn).

Citric acid concentration study (1:3 ratio to KOH)

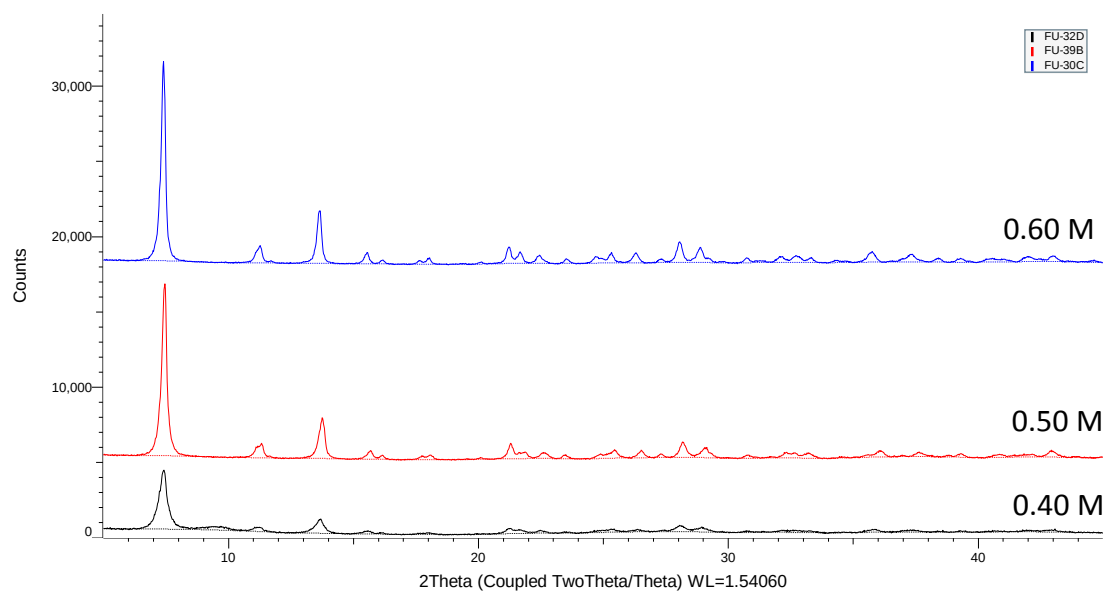


Figure S2: PXRD patterns of UTSA-16(Zn) synthesised from citric acid concentrations between 0.4 M and 0.6 M (ratio of citric acid:KOH maintained at 1:3).

KOH concentration study

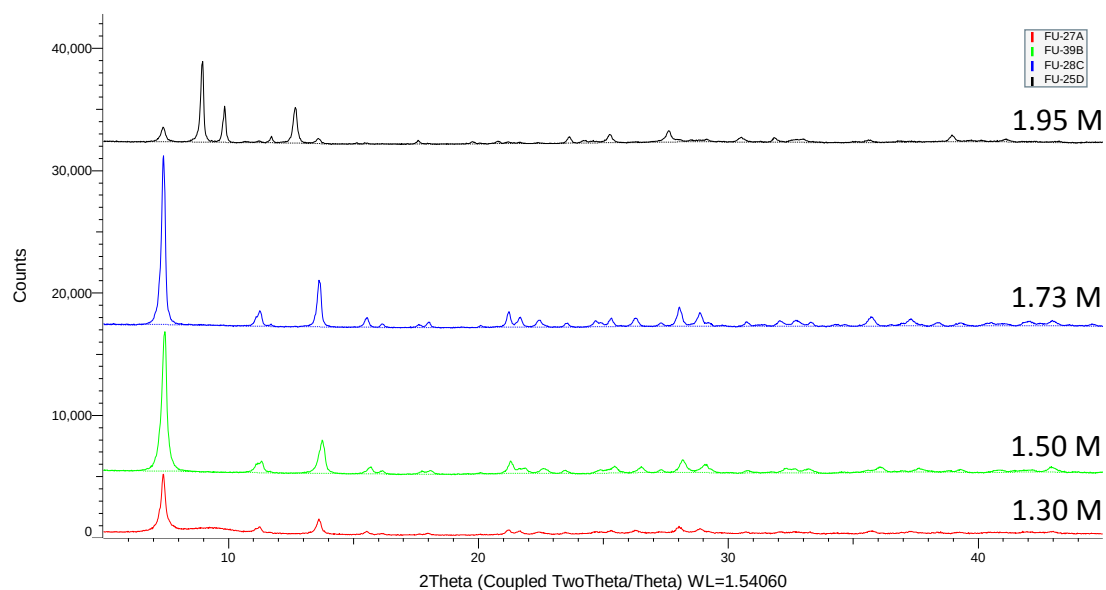


Figure S3: PXRD patterns of UTSA-16(Zn) synthesised from KOH concentrations between 1.30 M and 1.95 M.

Zn/Mg mixed-metal study

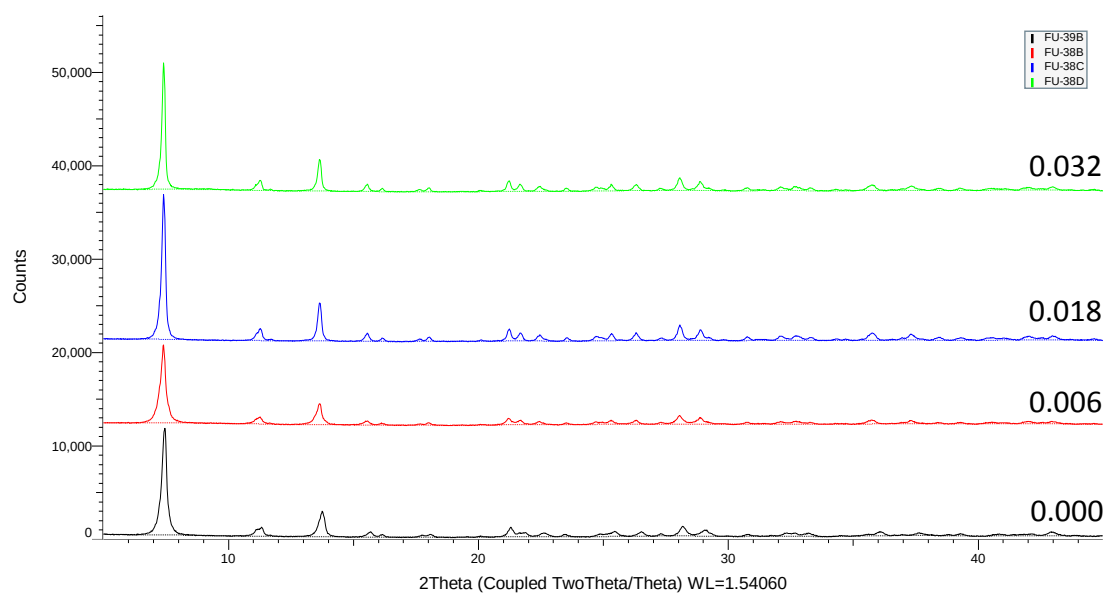


Figure S4: PXRD patterns of UTSA-16(Zn,Mg) synthesised with Mg metal mole fractions between 0 and 0.032 in the products.

Solvent ratio H₂O:EtOH study

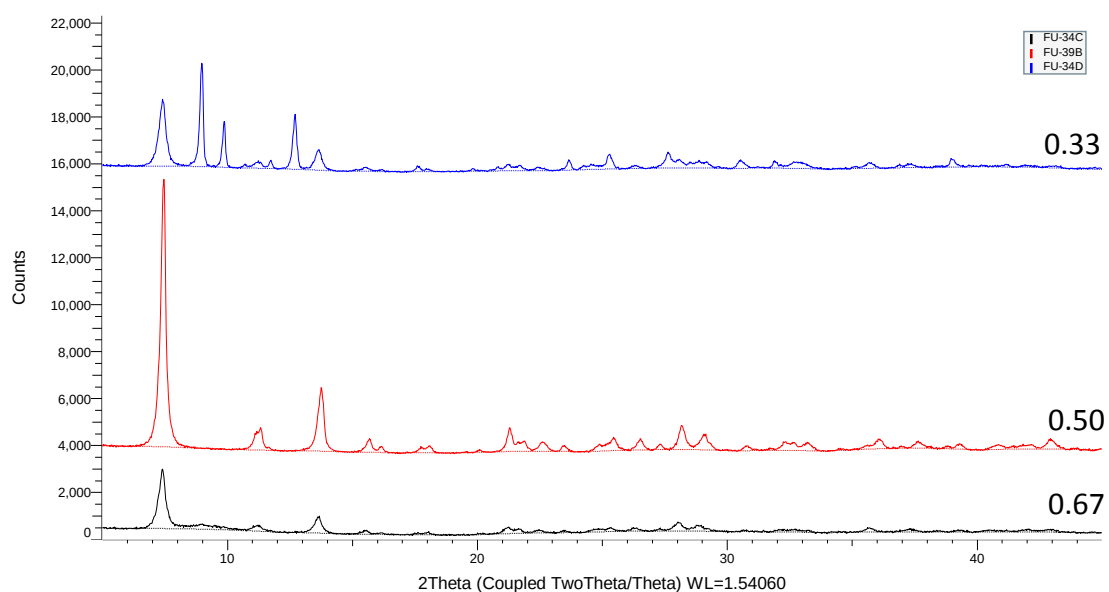


Figure S5: PXRD patterns of UTSA-16(Zn) synthesised from solvent fractions of H₂O in EtOH between 0.33 and 0.67.

Total pumps flow rate study

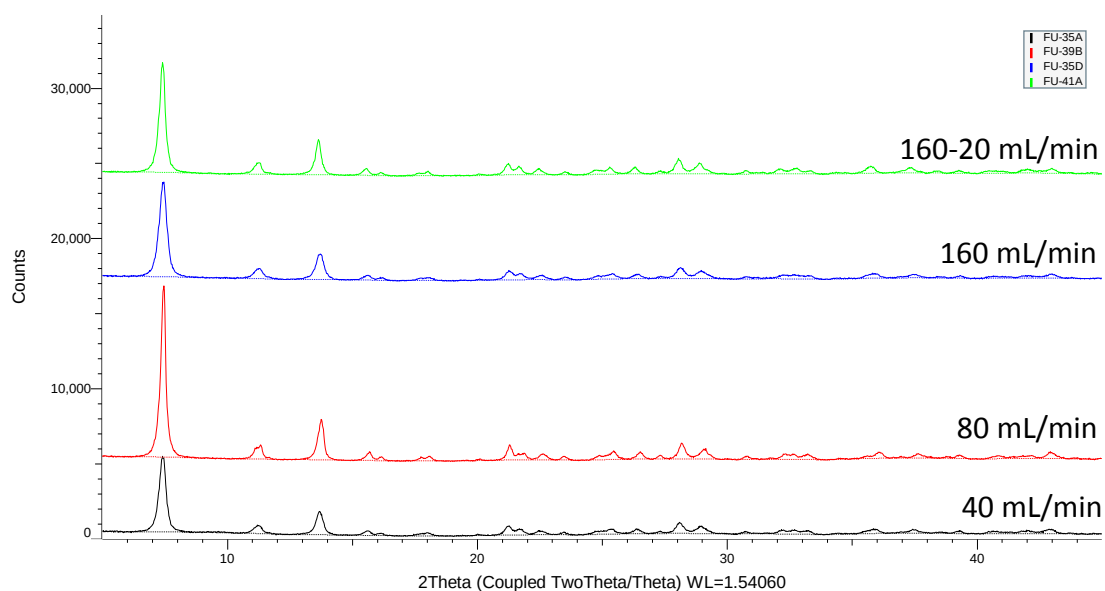


Figure S6: PXRD patterns of UTSA-16(Zn) synthesised from flow rates between 40 mL/min and 160 mL/min. The '160-20 mL/min' sample was mixed in the reactor at 160 mL/min, fed through the heater coil at 20 mL/min, then collected at 160 mL/min.

Water bath temperature study

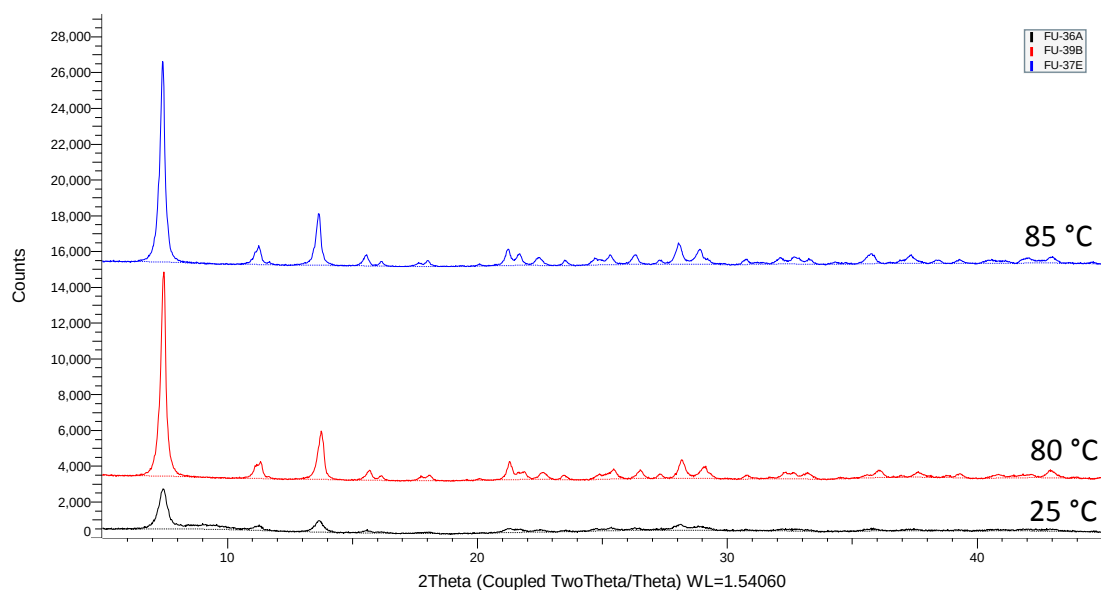


Figure S7: PXRD patterns of UTSA-16(Zn) synthesised from temperatures between 25 °C and 85 °C.

Scale-up and extra washing study

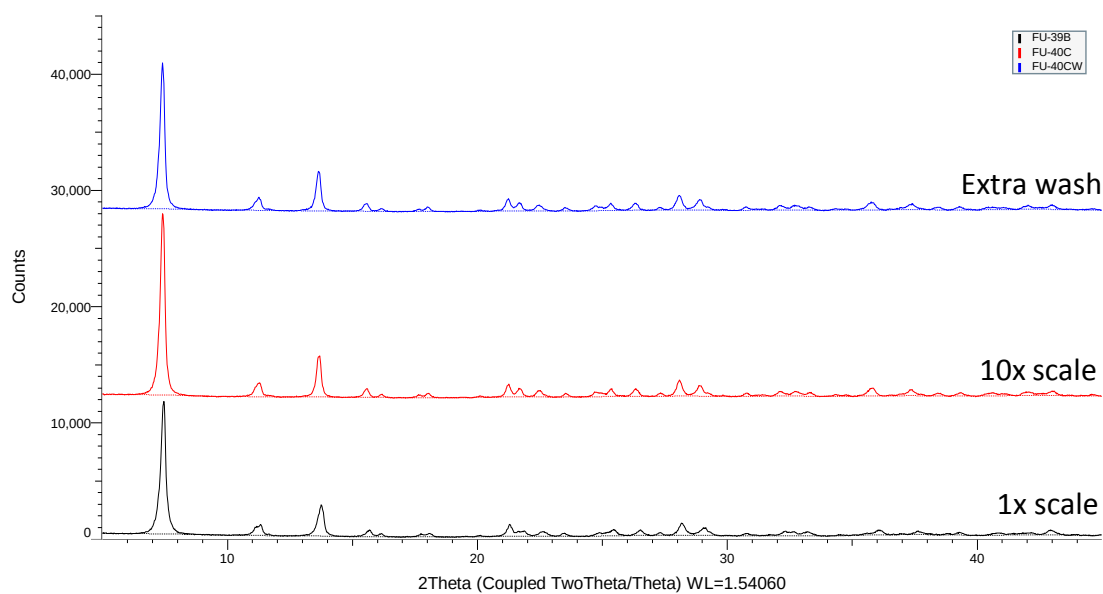


Figure S8: PXRD patterns of UTSA-16(Zn) at 1x and 10x scale, and a sample of the 10x scale subject to extra washing of 6 additional solvent exchanges over 5 days.

Incorporation of MNP-CA study

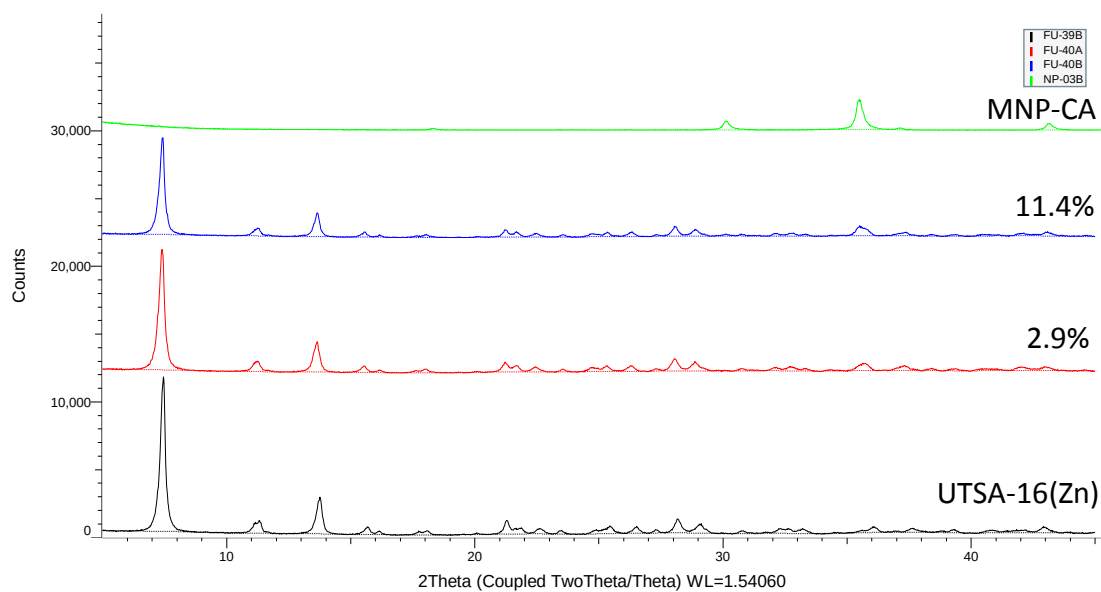


Figure S9: PXRD patterns of pristine UTSA-16(Zn), UTSA-16(Zn)@MNP-CA with MNP-CA concentrations of 2.9% and 11.4%, and pristine MNP-CA.

Thermal decomposition of UTSA-16(Zn) and MFCs

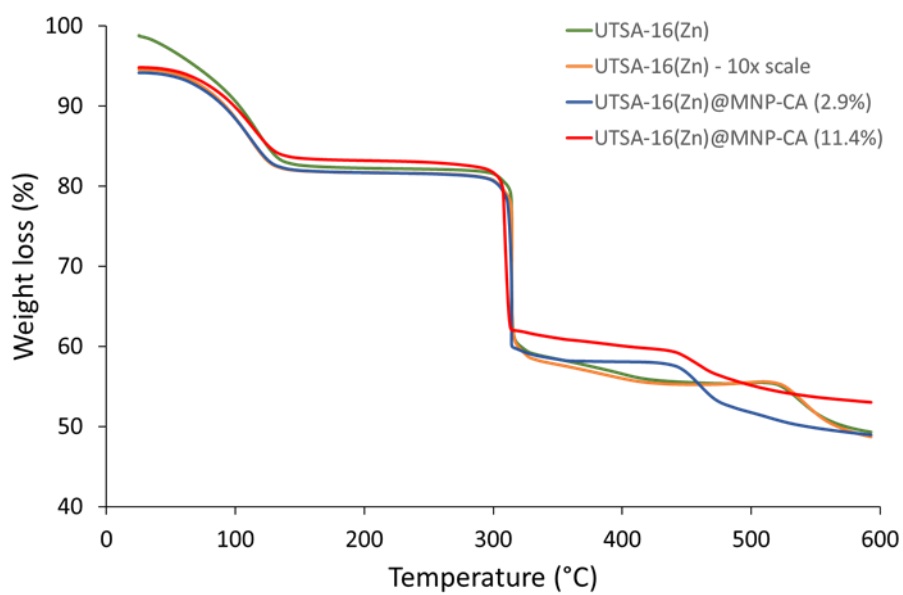


Figure S10: TGA thermograms showing thermal decomposition of UTSA-16(Zn) and 1x and 10x scale, and UTSA-16(Zn)@MNP-CA with 2.9% and 11.4% loadings of MNP-CA. Measurements conducted under air at a ramp rate of 10 °C/min.

SEM/EDX micrographs of UTSA-16(Zn) and analogues

Solvent ratio, flow rate and Zn/Mg mixed-metal studies

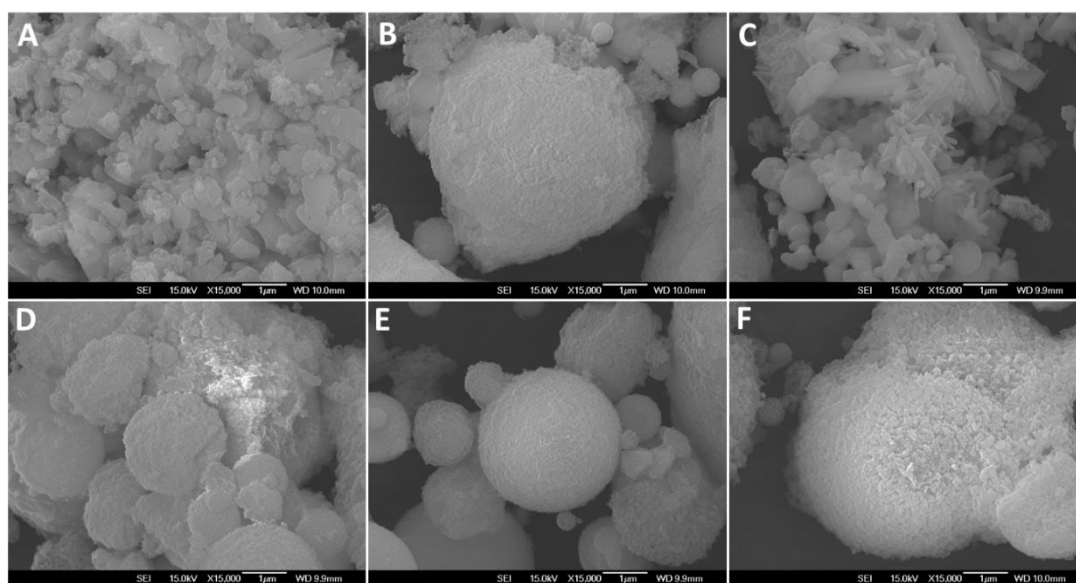


Figure S11: SEM micrographs of UTSA-16(Zn) synthesised from A: 0.67 H₂O solvent fraction, B: 0.5 H₂O solvent fraction & 80 mL/min flow rate, C: 0.33 H₂O solvent fraction, D: 40 mL/min flow rate, E: 160 mL/min flow rate, F: UTSA-16(Zn,Mg) with 0.2 mole fraction Mg in reactants.

Scale-up and extra washing study

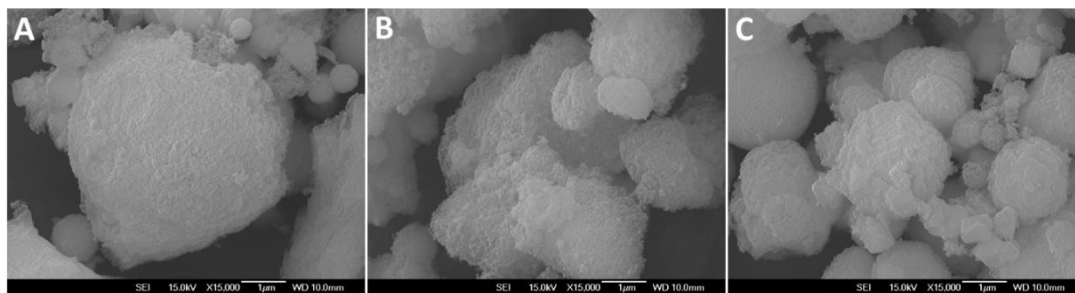


Figure S12: SEM micrographs of UTSA-16(Zn) synthesised at A: 1x scale, B: 10x scale, C: 10x scale with extra washing of 6 additional solvent exchanges over 5 days.

Incorporation of MNP-CA study

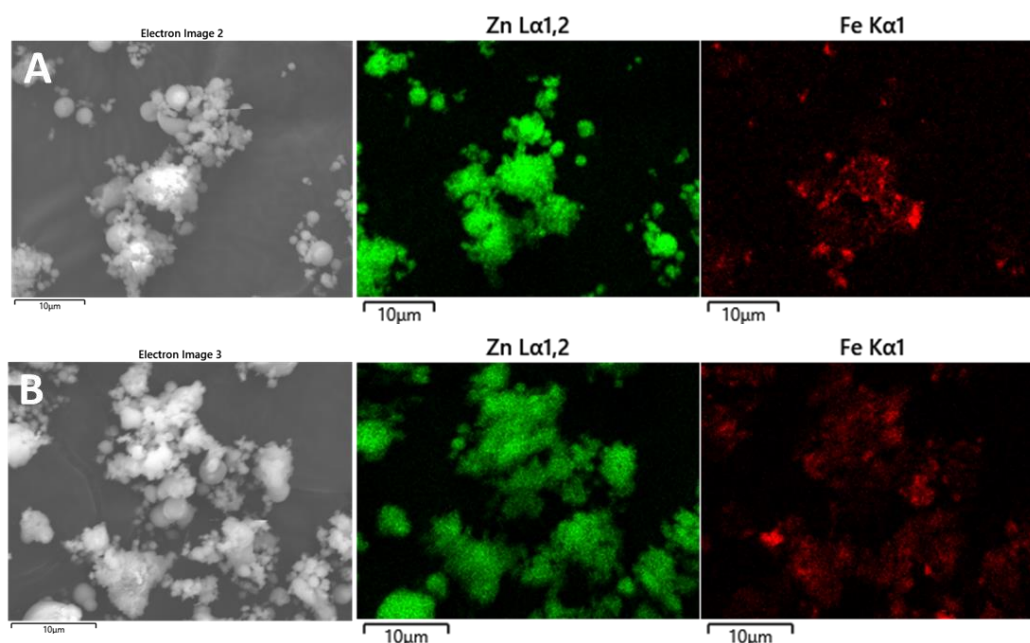


Figure S13: SEM micrographs including EDX elemental analysis of UTSA-16(Zn)@MNP-CA MFCs. A: UTSA-16(Zn)@MNP-CA (2.9%), B: UTSA-16(Zn)@MNP-CA (11.4%). Green shows the presence of Zn in the MOF structure, and red evidences the distribution of Fe from MNP-CA.

Appendix 5

2nd author papers:

- Molinar-Díaz J., **Woodliffe J. L.**, Steer E., Morley N. A., Brown P. D., Ahmed I.; *Optimisation of the Flame Spheroidisation Process for the Rapid Manufacture of Fe₃O₄-Based Porous and Dense Microspheres*; *Molecules*, 2023, 28(6), 2523, <https://doi.org/10.3390/molecules28062523>
- Molinar-Díaz J., **Woodliffe J. L.**, Milborne B., Murrell L., Islam M. T., Steer E., Weston N., Morley N. A., Brown P. D., Ahmed I.; *Ferromagnetic Cytocompatible Glass-Ceramic Porous Microspheres for Magnetic Hyperthermia Applications*; *Advanced Materials Interfaces*, 2023, 2202089, <https://doi.org/10.1002/admi.202202089>

Key contributions:

- *Conceptualisation of magnetic field heating experiments to demonstrate suitability of magnetic particles for magnetic hyperthermia treatment*
- *Development of magnetic induction heating set-up to measure the temperature rise of samples under an alternating magnetic field*
- *Performance of an experimental induction heating investigation on magnetic particles targeting a controlled temperature ramp and isothermal hold at 40-45 °C*

Alternative applications of induction heating

Context

To test the magnetic field heating capabilities of the magnetic microspheres and MFCs produced as described in Chapters 2-4, an induction heating experimental set-up was developed. As detailed in the experimental sections of Appendices 2-4 (e.g. page: 120) and in Chapter 2 Figure 4 (page: 19), this involved an induction heater with water-cooled copper coil attachment, a fibre optic thermocouple with a data logger and a borosilicate glass sample tube. The two papers listed above detail investigations into ferromagnetic Ca₂Fe₂O₅ and P40-Fe₃O₄ (P40: 40P₂O₅-16CaO-

24MgO-20Na₂O) glass-ceramic microspheres for alternate applications. These investigations were led by a colleague, Dr Jesús Molinar-Díaz, who was targeting biomedical applications for the materials, particularly magnetic induced hyperthermia. This application required rapid and controlled induction heating of magnetic particles up to 40-45 °C to induce cell death in cancerous regions of the body. In collaboration with Jesús, magnetic field heating investigations were conducted, using the induction heating analysis set-up developed for the MFCs. The results were very positive, demonstrating the controlled heating of both sets of materials and their suitability for magnetic hyperthermia applications.

Summary

Ca₂Fe₂O₅ microspheres

The paper entitled *“Optimisation of the Flame Spheroidisation Process for the Rapid Manufacture of Fe₃O₄-Based Porous and Dense Microspheres”* details a rapid flame spheroidisation process developed to produce compositionally uniform and ferromagnetic Ca₂Fe₂O₅ porous and dense microspheres. The effects of Fe₃O₄:CaCO₃ mass ratios and O₂/C₂H₂ gas flow settings on particle morphologies and compositions were studied. A 1:1 mass ratio and 2:2 gas flow setting were optimal for producing microspheres with compositional uniformity (MLA study). Suitability of the microspheres for magnetic hyperthermia applications was demonstrated through magnetisation measurements and an induction heating study, showing controlled temperature increase to 42.4 °C over 40 s using an alternating magnetic field.

P40-Fe₃O₄ microspheres

The paper entitled: *“Ferromagnetic Cytocompatible Glass-Ceramic Porous Microspheres for Magnetic Hyperthermia Applications”* describes an investigation into the manufacture of highly porous and cytocompatible P40-Fe₃O₄ glass-ceramic microspheres via a flame spheroidisation process. The materials contained distributions of ≈10 µm sized Fe₃O₄ and Ca₂Fe₂O₅ domains embedded within 125-212 µm sized P40-based microsphere glass matrices. Magnetisation measurements and an induction heating study demonstrated the suitability of the microspheres for magnetic hyperthermia applications, showing controlled temperature increase to

41.9 °C using an alternating magnetic field. The cytocompatibility was confirmed through human osteoblast-derived cell-culture investigations.