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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	*N,N*-Diethylformamide
dhtp	6,6′-Dihydroxy terpyridine
DMA	*N,N*-Dimethylacetamide
DMF	*N,N*-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	Isoreticular 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(*p*-benzoicacid)pyrene
TC-TTF	Tetra(carboxyl)tetrathiafulvalene
TCPP(H_2)	Tetrakis(4-carboxyphenyl)porphyrin
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TPDC	*p*-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

Contents

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 BASF[10] and university spin out companies producing industrially relevant quantities[11] 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 Package[30] 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]

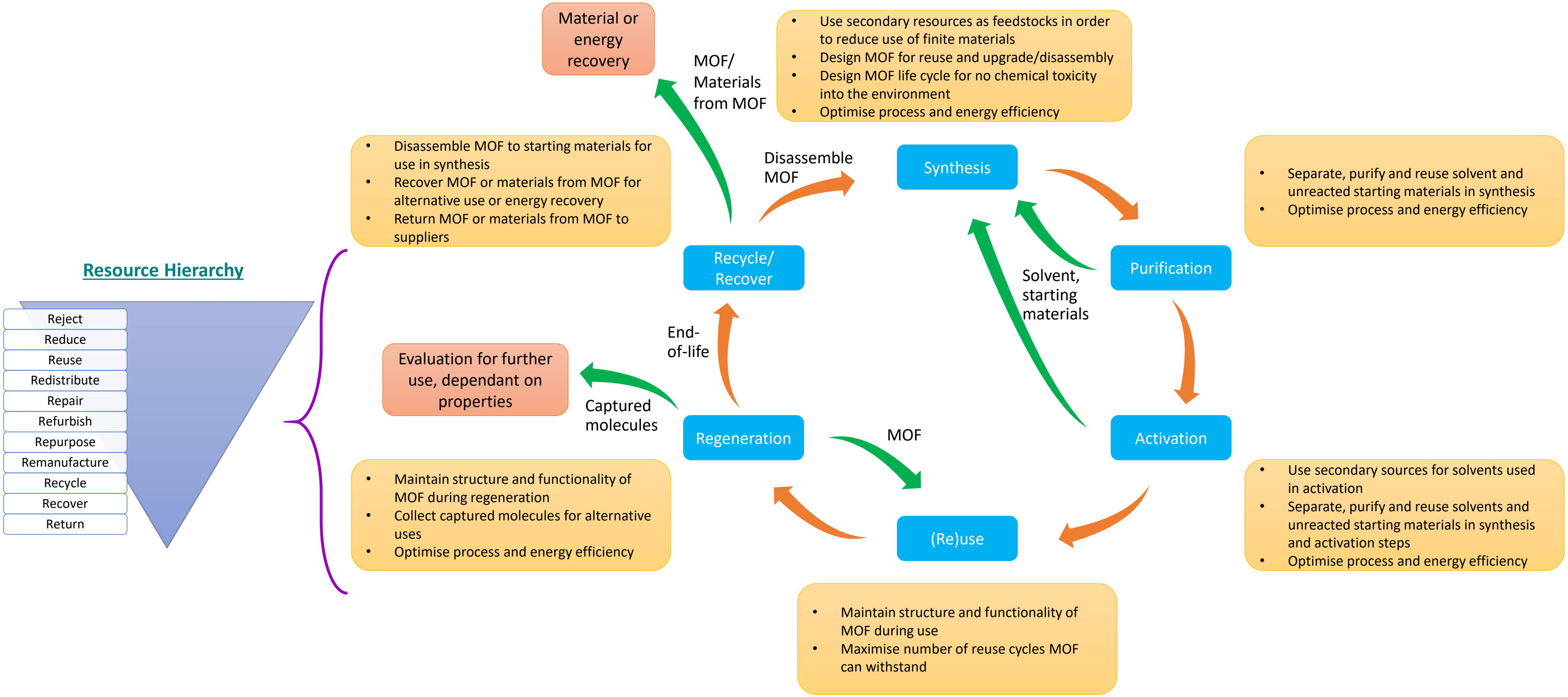
- Reuse has been shown to be less demanding on the environment, requiring fewer resources, less energy and less labour when compared with the manufacturing of a product from virgin materials, recycling or disposing.[36] With respect to MOFs, the reuse principle could be applied by collecting the solvent 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 chemistry[46] 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 industry[49] and also elsewhere in the chemical industry[50] 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 CO_2 could be collected upon regeneration and used as a chemical feedstock.[51]



- Use secondary resources as feedstocks in order to reduce use of finite materials
- Design MOF for reuse and upgrade/disassembly
- Design MOF life cycle for no chemical toxicity into the environment
- Optimise process and energy efficiency

- Disassemble MOF to starting materials for use in synthesis
- Recover MOF or materials from MOF for alternative use or energy recovery
- Return MOF or materials from MOF to suppliers

- Separate, purify and reuse solvent and unreacted starting materials in synthesis
- Optimise process and energy efficiency

- Maintain structure and functionality of MOF during regeneration
- Collect captured molecules for alternative uses
- Optimise process and energy efficiency

- Use secondary sources for solvents used in activation
- Separate, purify and reuse solvents and unreacted starting materials in synthesis and activation steps
- Optimise process and energy efficiency

- Maintain structure and functionality of MOF during use
- Maximise number of reuse cycles MOF can withstand

Figure 1: A representation of circular and sustainable opportunities in a MOF life cycle, applying principles of 'circular chemistry' including the 'Resource Hierarchy' ladder[25]

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 CO_2, 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.

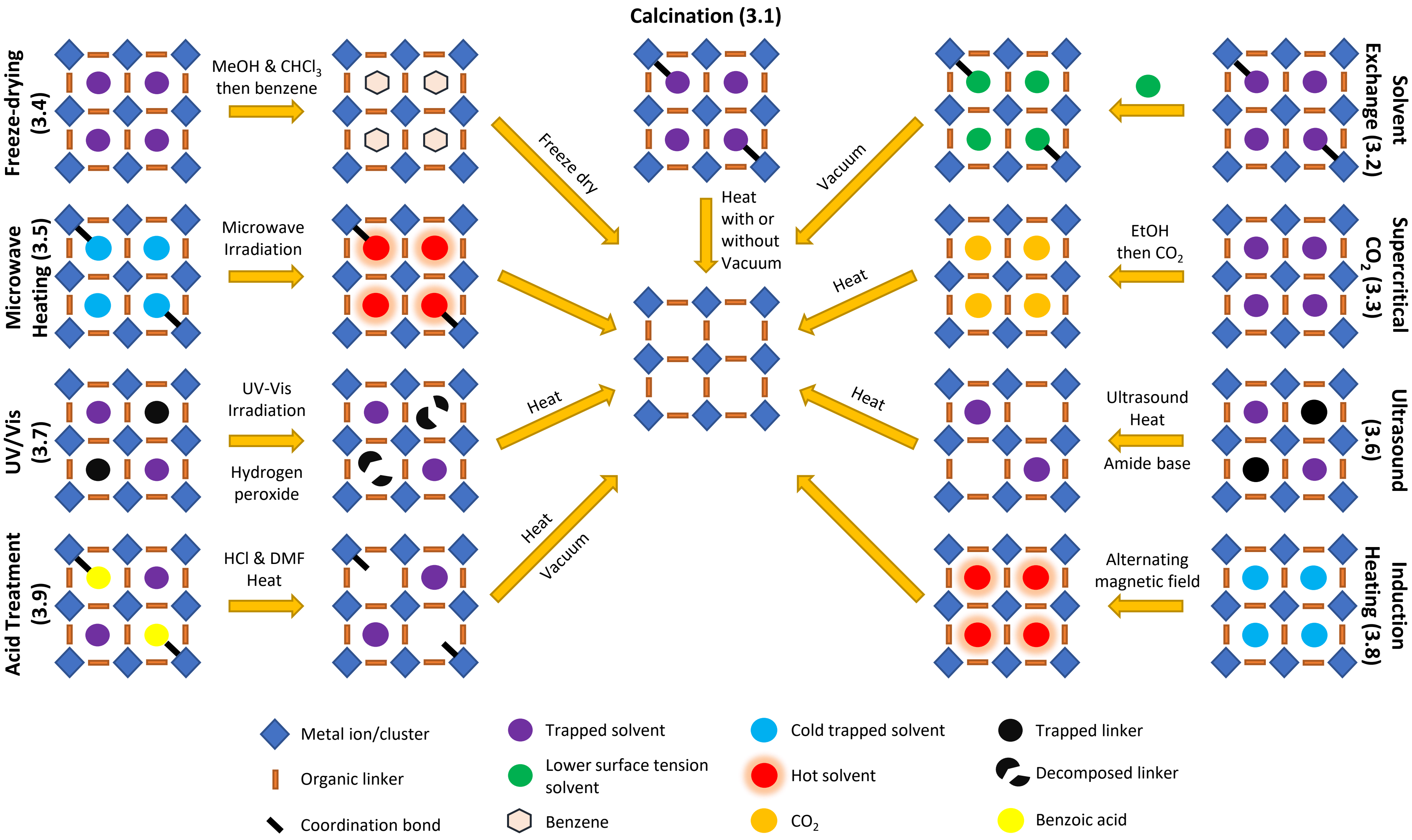


Figure 2: Simplified overview of representative purification and activation techniques including their corresponding sections in this review in brackets

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 [$Zr_6O_4(OH)_4$] clusters with BDC struts, activated at 300 °C),[57] Zn(BDC) (activated at 140 °C and 5×10^{-5} Torr),[58] and $Ni_2(4,4'\text{-bipy})_3(NO_3)_4$ (activated at 100 °C).[59] In other cases solvent removal has been shown to cause an advantageous change in crystal structure, *e.g.* $[Co^{II}(H_2O)_6]H_2(\text{TC-TTF})\cdot 2H_2O$.[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 1 D rhombic-shaped tunnels of Al(OH)(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 H_2BDC molecules are effectively removed at 400 °C for MIL-53(Al);[62] however, MIL-53(Cr) and MIL-53(V), both also containing H_2BDC, 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 hours[67], and $Cu_3(BTC)_2$ (HKUST-1) also requires heating at 200 °C.[68] Even recently reported MOFs such as $[Al_2(OH)_2(C_{16}O_8H_6)](H_2O)_6$ (NOTT-300/MFM-300), promising in NO_2, SO_2 and CO_2 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 $Co_2(dhtp)$ and $Zn(mIM)_2$ (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 $Zn_4O(BDC)_3$ (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 $Zr_6(\mu_3\text{-}OH)_8(OH)_8TBAPy)_2$ (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 $Zn_4O(H_2N\text{-}BDC)_3$ (IRMOF-3) and $Zn_4O(TPDC)_3$ (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 Zn_4O(naphthalene-2,6-dicarboxylate)$_{1.5}$(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 m^2g^{-1} compared to the theoretical value of 4900 m^2g^{-1} (calculated from its structure).[79] When solvent exchanged with *n*-hexane (surface tension: 17.9 mNm^{-1}), a higher surface area of 4980 m^2g^{-1} was obtained, close to the predicted theoretical value.[18] Similar results were observed for MOF $Zn_6(btb)_4(4,4'\text{-bipy})_3(DMF)_{55}(H_2O)_{32}$ (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 m^2g^{-1}. When perfluoropentane was used, a surface area of 4890 m^2g^{-1} was measured, comparable to the theoretical value of 4741 m^2g^{-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 Zn_4O metal clusters (MOF-5, UMCM-9, and $[Zn_4O(CVB)_3]\cdot 13(DEF)\cdot 2H_2O$ (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 $Cu_2(BDC)_2$ (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 m^2g^{-1} compared to 1740 m^2g^{-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, Ni_2(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 CO_2 (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 CO_2. The CO_2-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 $Cu_3(C_{60}H_{24}O_{12})(H_2O)_3$ (also known as NU-100), which features a hexa-carboxylated 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 m^2g^{-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 m^2g^{-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 CO_2 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 CO_2 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,

$Cr_3OF(H_2O)_2(BDC)_3$ (MIL-101(Cr)) shows a similar BET surface area after purification in 1 M NH_4F solution at 70 °C for 24 hours followed by activation at 100 °C under vacuum overnight when compared to SCD (3350 m^2g^{-1} and 3400 m^2g^{-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 m^2g^{-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 CO_2 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 CO_2, which may also have a potentially negative impact on the sustainability of the technique. CO_2 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 CO_2 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 m^2g^{-1} for compound 1 and 2, respectively) compared to solvent exchange then vacuum-drying at 60 °C overnight (526 and 791 m^2g^{-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, $[Zn_2L(\text{imidazole})]\cdot 7(\text{DMF})$ where L = Tris((4-carboxyl)phenylduryl)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 food[101] and biopharmaceutical[102] 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 carbon[109]) 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 m^2g^{-1} (as synthesised) to 1467 m^2g^{-1} (after first extraction) and 2019 m^2g^{-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 m^2g^{-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 $Zr_6O_4(OH)_4(BTC)_2(COOH)_6$, MOF-808; $Zr_6O_8(NDC)_3(CH_3COO)_2(C_2H_5OH)_7(DMF)$, 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-53[61] 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 H_2BDC linkers from selected MOFs in the MIL-series.[120] The authors showed that MIL-53(Al) containing unreacted H_2BDC 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 it's analogue $Al(OH)(fum)\cdot 3.5H_2O$ (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 m^2g^{-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 H_2BDC, 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 H_2BDC 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 H_2BDC observed within 60 minutes. After filtration, thermogravimetric analysis showed that both DMF (the synthesis solvent) and H_2BDC 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 m^2g^{-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 m^2g^{-1} *c.f.* 1580 m^2g^{-1}; ZIF-8: 1130 m^2g^{-1} *c.f.* 1400-1500 m^2g^{-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 H_2BDC 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 production[35] 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 Zr_6 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, $Zr_6(\mu_3\text{-}O)_8(OH)_8(TCPP)_2$ (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; $Ni_2(4,4'\text{-bipy})_3(NO_3)_4$; $[Co^{II}(H_2O)_6]H_2(TC\text{-}TTF)\cdot 2H_2O$	DMF; H_2O	✓	✓	✗	✓	57–60,67
Solvent Exchange (3.2)	MOF-5; $Co_2(dhtp)$; ZIF-8; NU-1000; IRMOF-3; IRMOF-16; UMCM-9; FJI-1; SNU-70; HKUST-1; Cu-MOF-2; Ni-MOF-74	DMF; DEF; Chlorobenzene; DMSO; MeCN; MeOH; EtOH; H_2O	✓	✓	✓	✓	18,53,67, 75–78,81–84
Supercritical CO_2 (3.3)	IRMOF-3; IRMOF-16; UMCM-9; NU-100; NU-109E; NU-110E	DMF	✗	✗	✓	✓	19,78,87–90
Freeze-drying (3.4)	$Cu_2(L)(H_2O)_2$[a]; FIR-3; HKUST-1	DMF; DEF; H_2O; 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_2O	✗	✓	✓	✓	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

[a] $L\text{-}H_4$: 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 CO_2 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 CO_2, 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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