Metal-Organic Frameworks as performant adsorbents for cultural heritage preservation

Training Activities - NEMOSINE

CNRS-Paris & IST-ULisboa
Speakers: Maria Neves and Cátia Freitas

GA760801 funded by

Metal-Organic Frameworks as performant adsorbents for cultural heritage preservation

Part I:

Maria Neves CNRS-Paris
maria-ines.severino-neves@espci.fr

GA760801 funded by

Part I. Synthesis and shaping MOFs

01 Adsorbents in cultural heritage

02 Metal-organic frameworks

03 Material synthesis

04 Shaping

Part II. Advance characterisation of MOFs materials

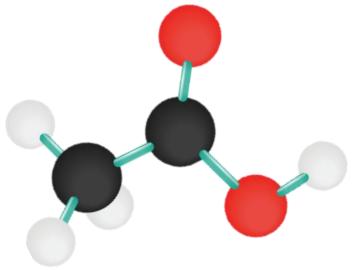
01 General considerations

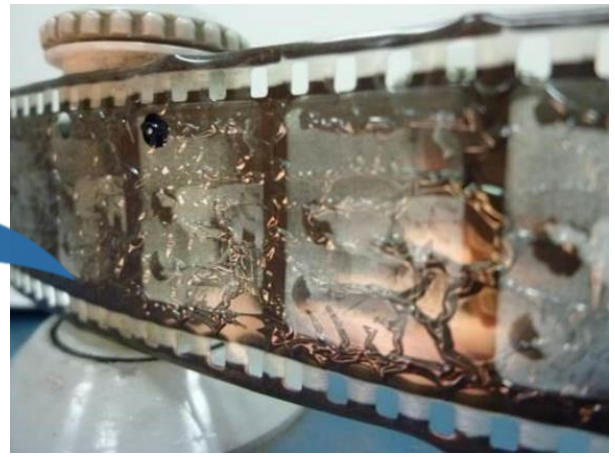
02 Advance characterisation

03 Acetic acid performance

04 Breakthrough

Vinegar Syndrome

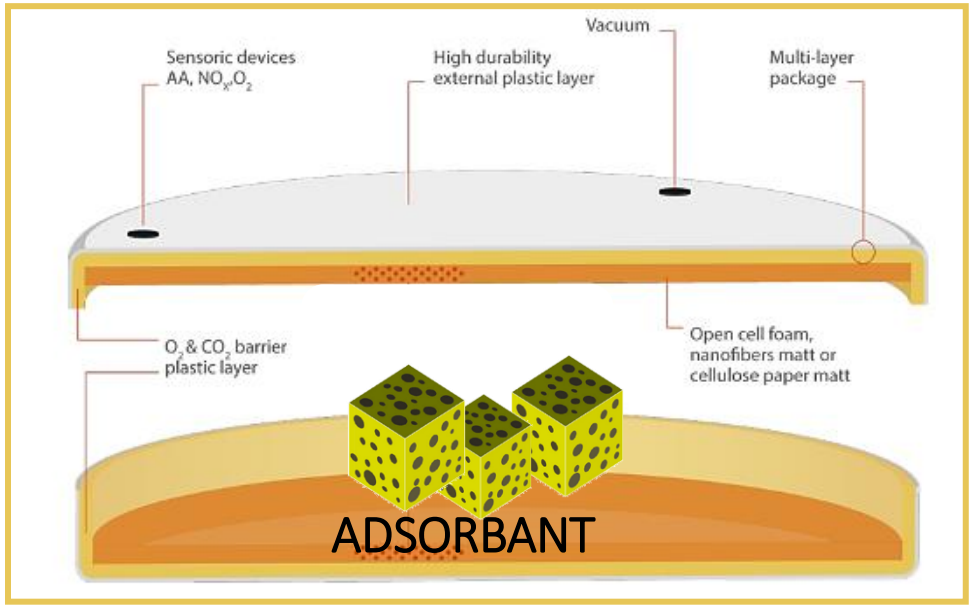




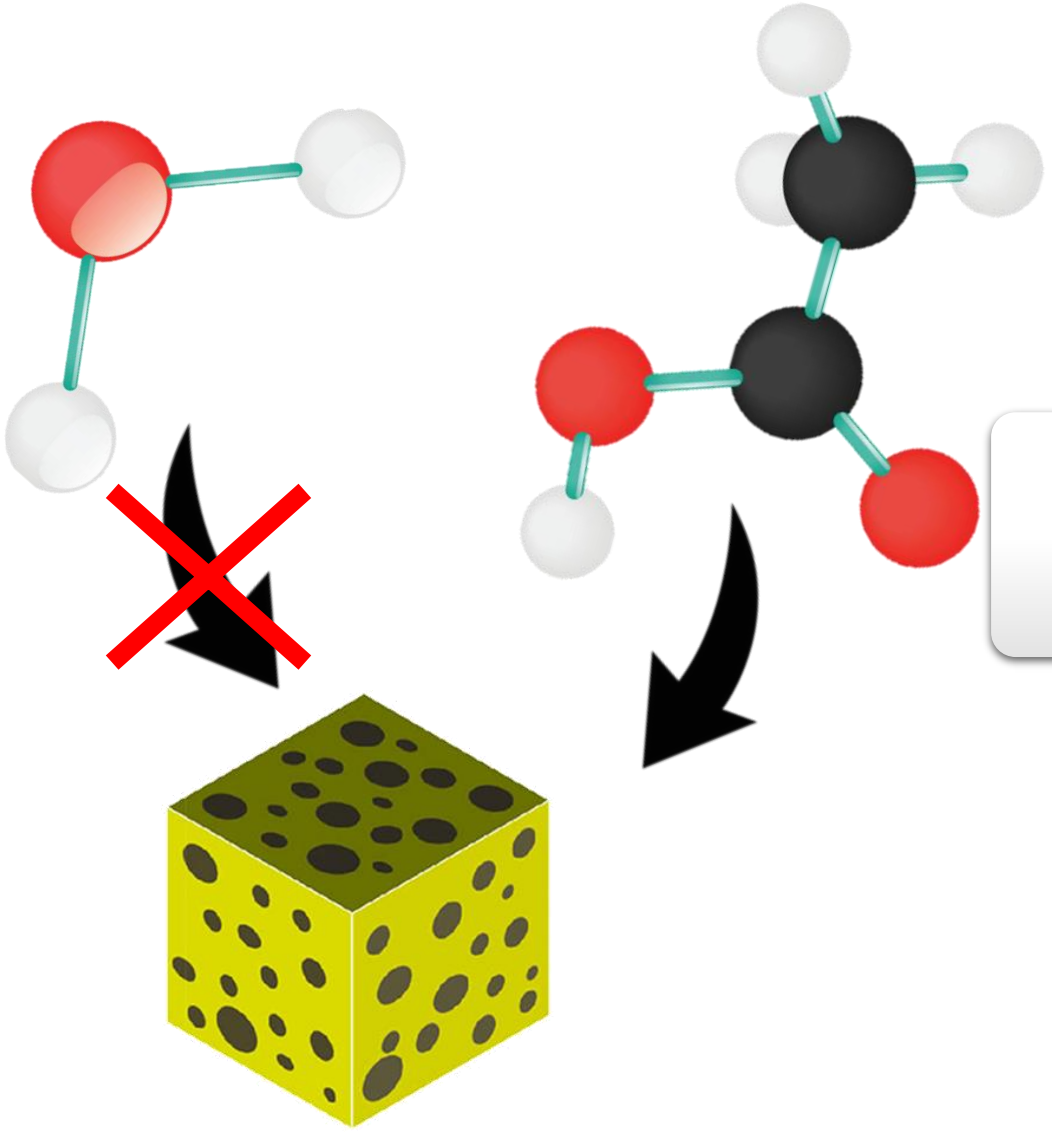
Refrigeration systems

ADSORBANT

Films Preservation



- STABILITY IN WATER
- HIGH ADSORPTION CAPACITY
- ACETIC ACID SELECTIVITY

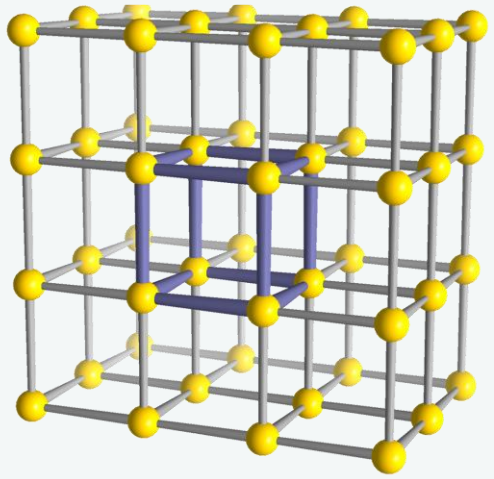


- Adsorbents
  - Zeolites
  - Activated carbons
  - Metal-Organic Frameworks (MOFs)

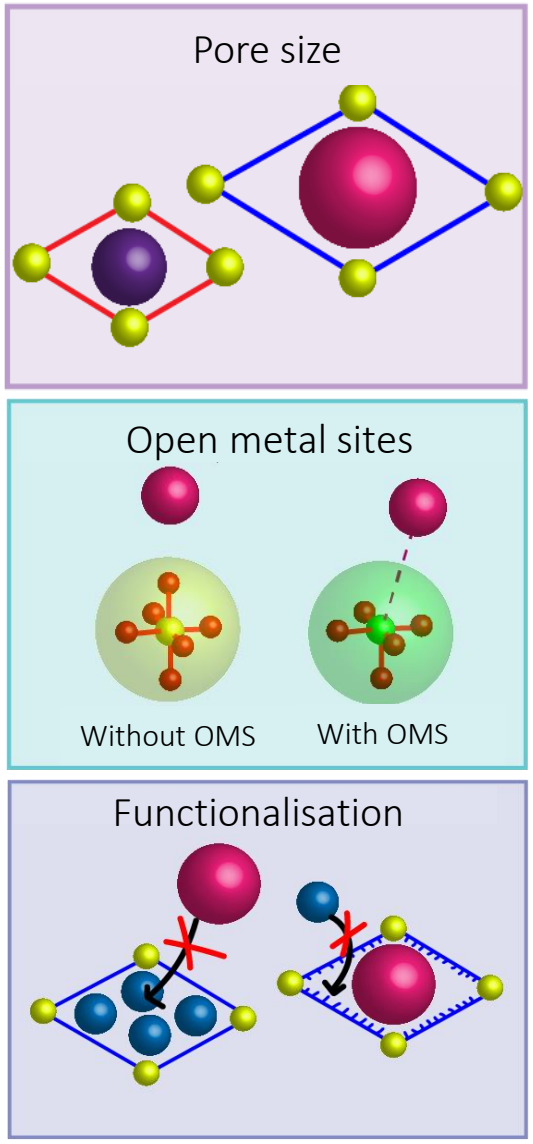
MOFs' pore size > 1 nm

Inorganic part
≡ Metal cation

Organic ligand
≡ Spacer

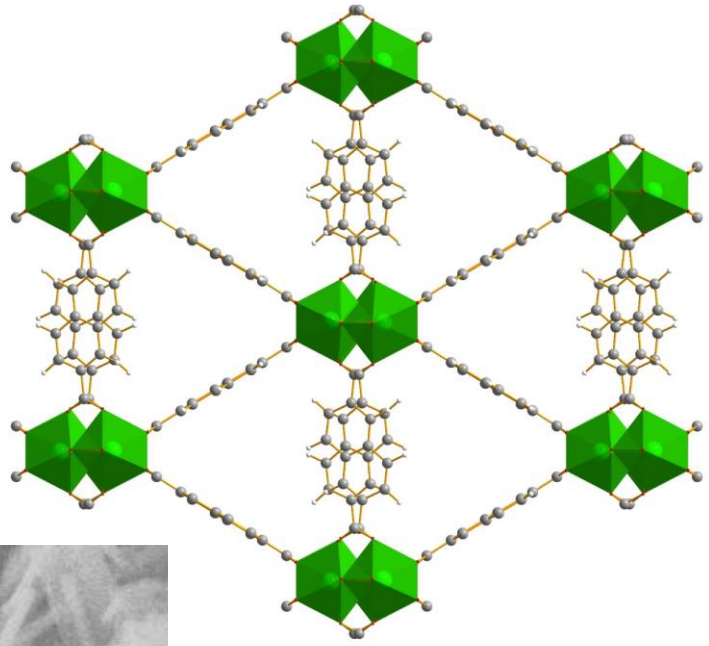


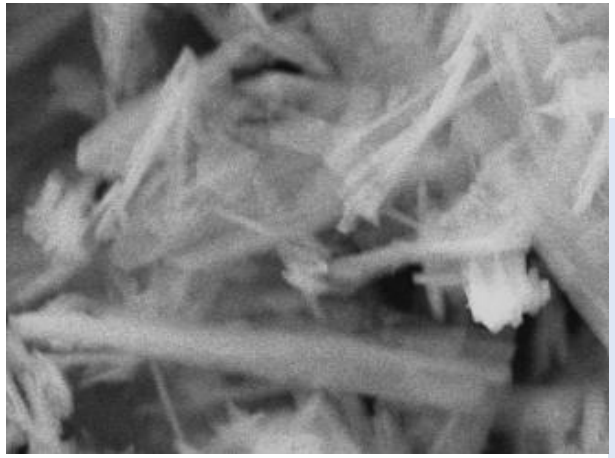
- High specific areas and porosity
- Tunability
- Low regeneration temperature



Properties

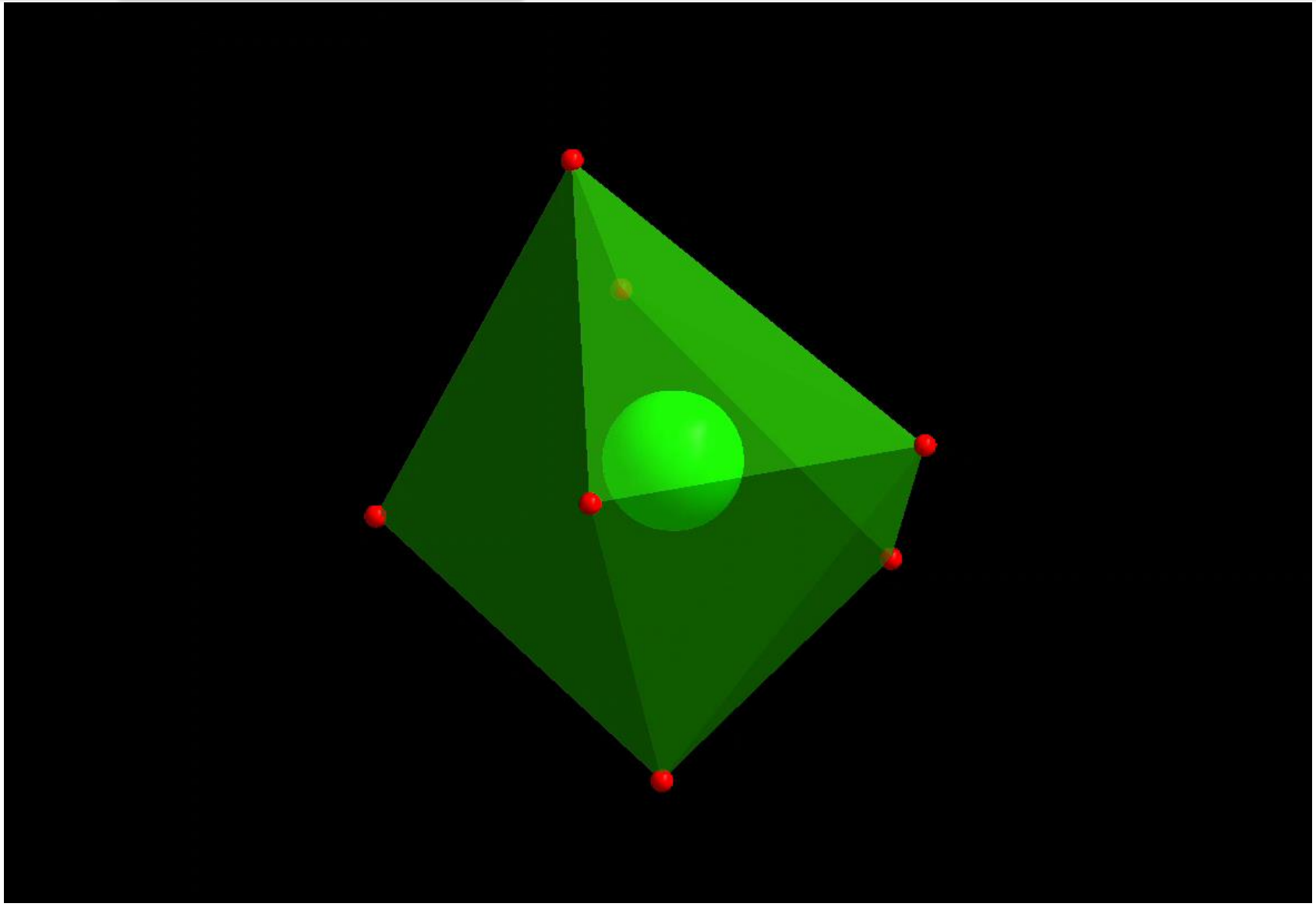
- Affinity
- **Hydrophobic/ hydrophilic balance**
- Etc.

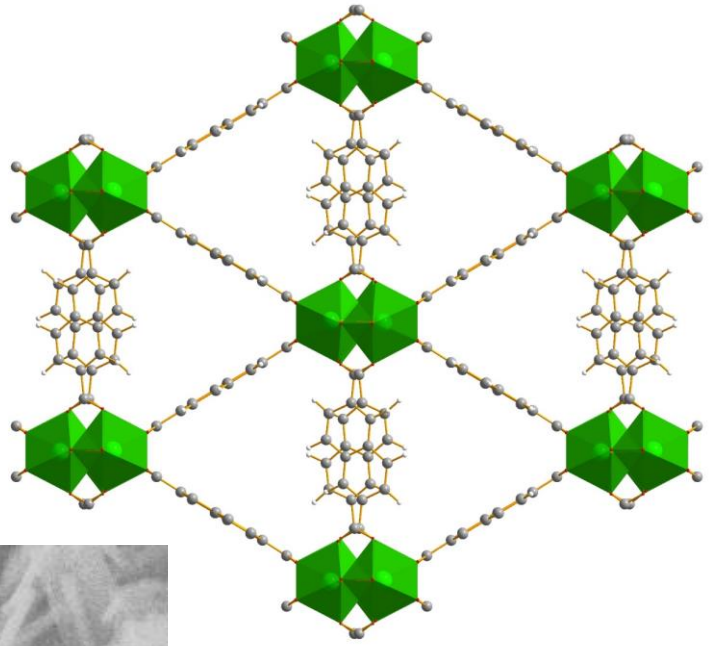


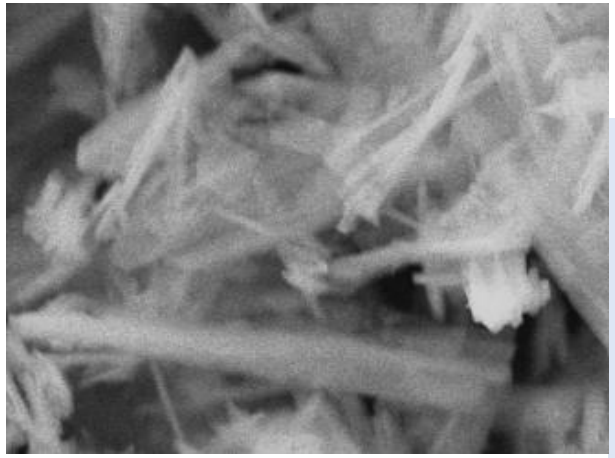


MIL-140B

- Hydrophobic MOF
- Absence of polar groups in the inorganic nodes (e.g., –OH)







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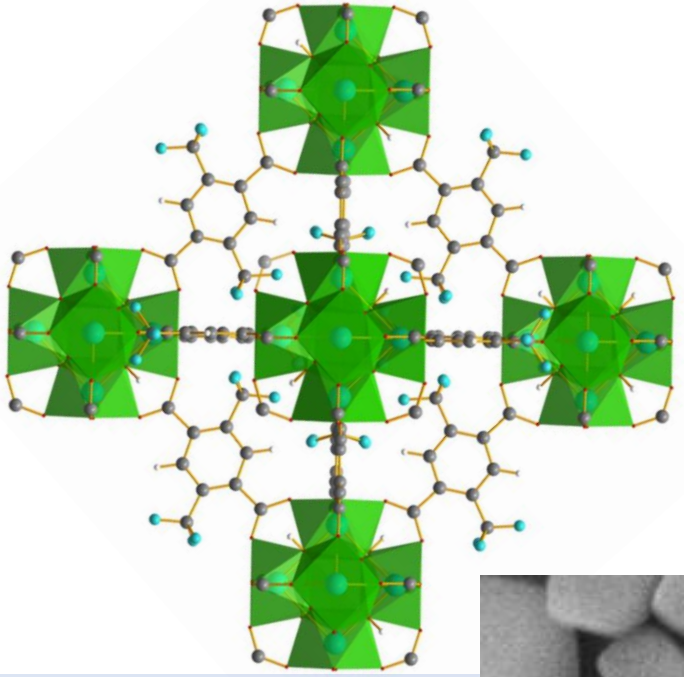
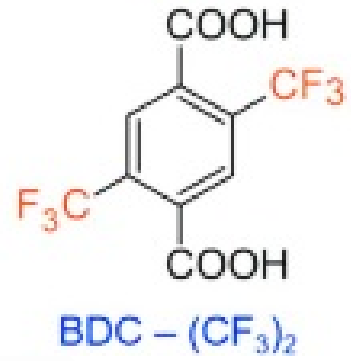
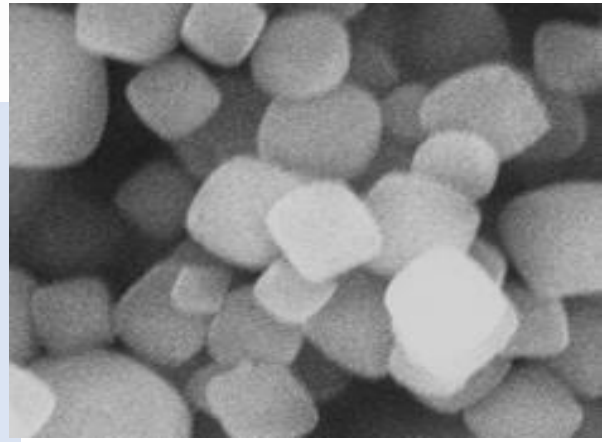
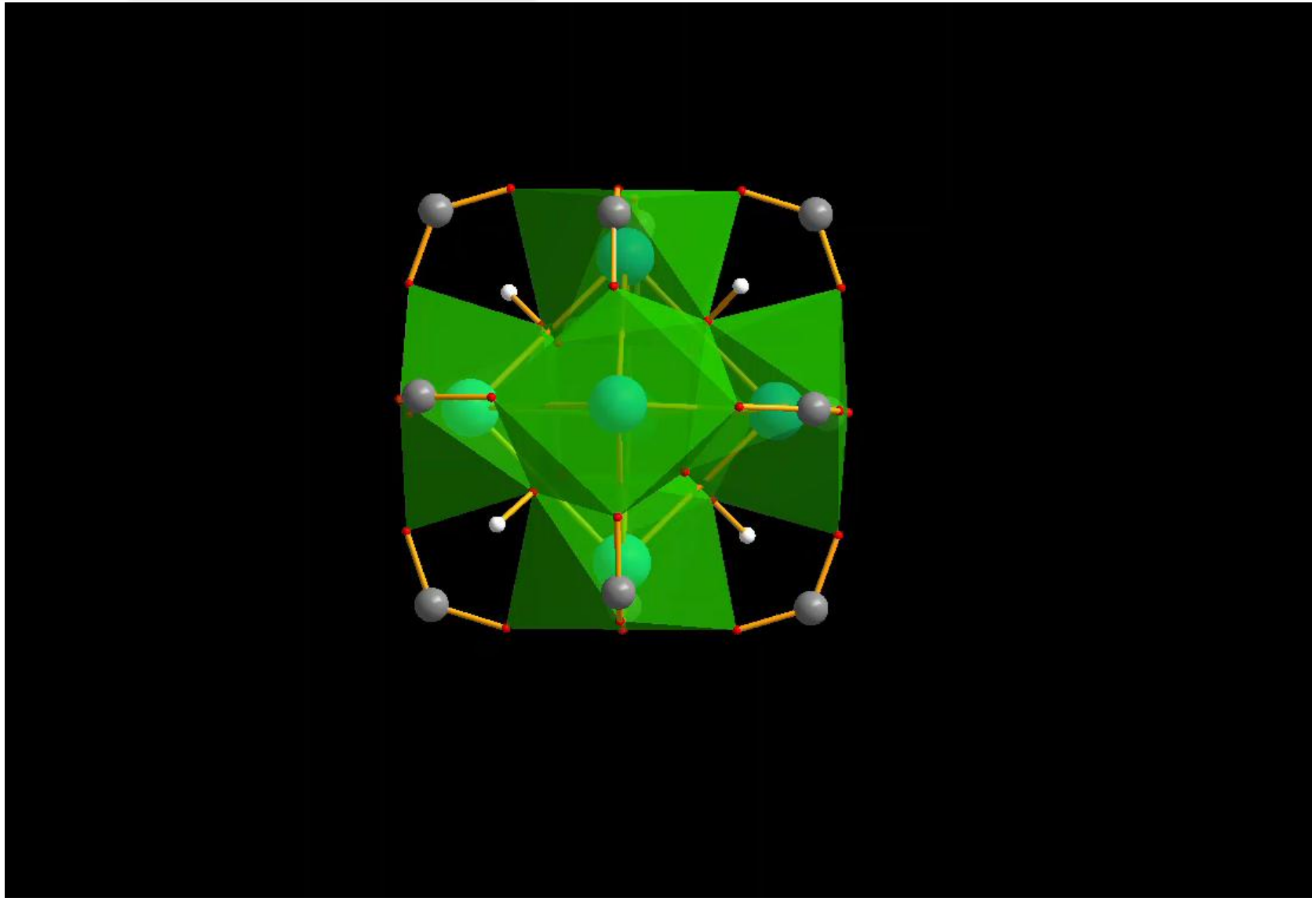


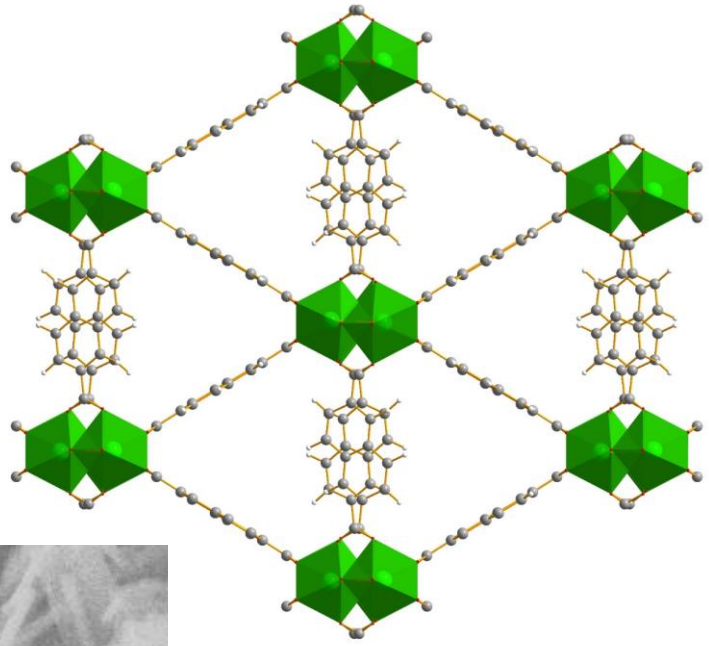


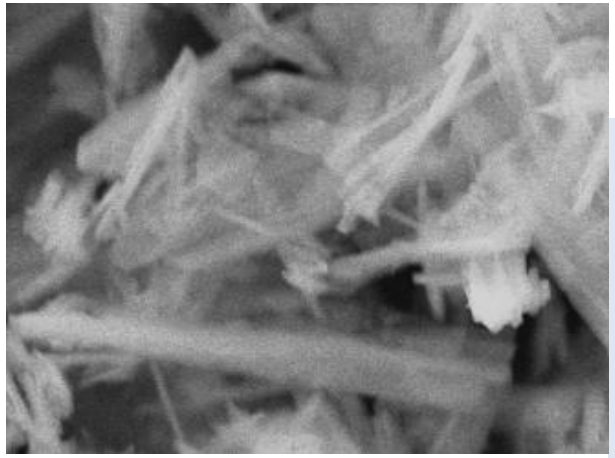
UiO-66-2CF_3

- Stable material
- Functionalized linker with hydrophobic groups (-CF_3)









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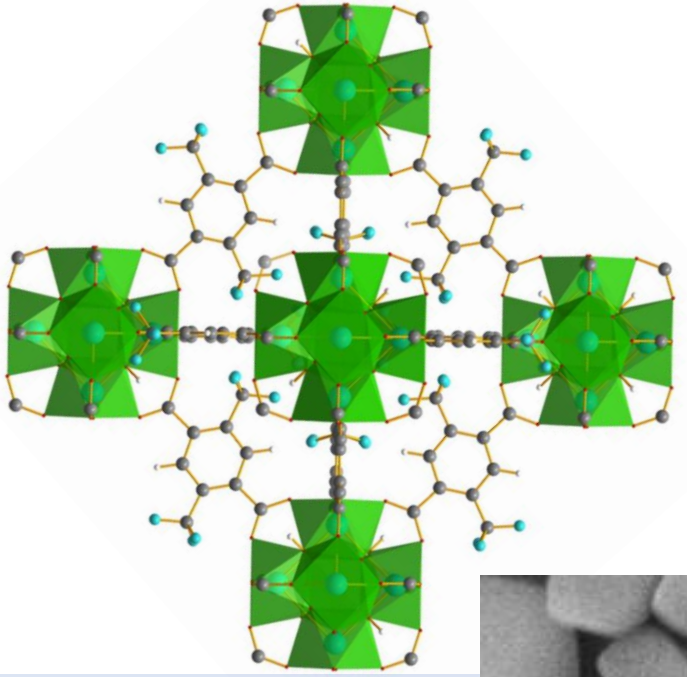

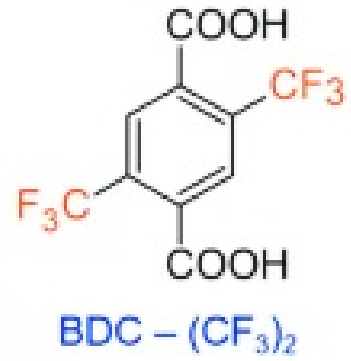

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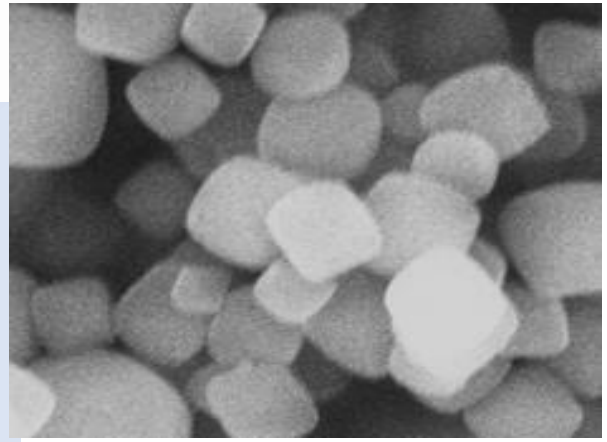
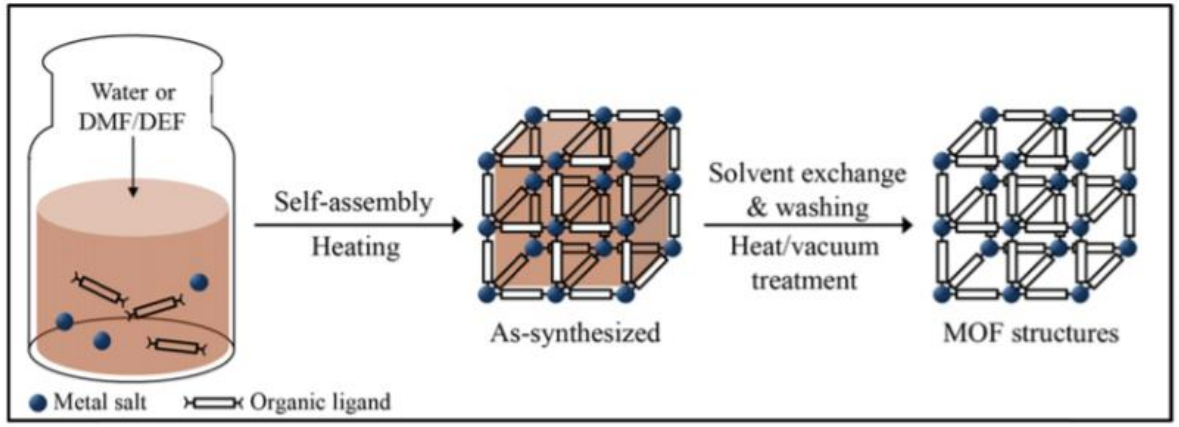
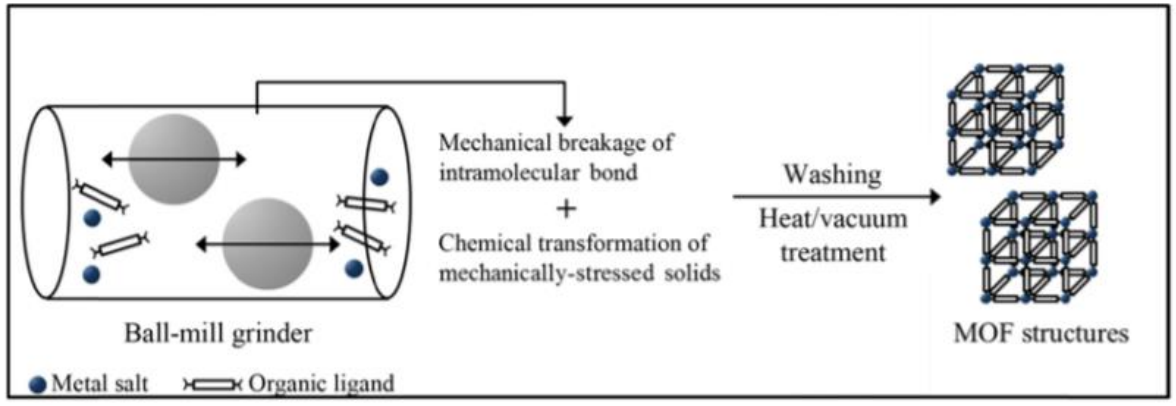


Hydrothermal/Solvothermal

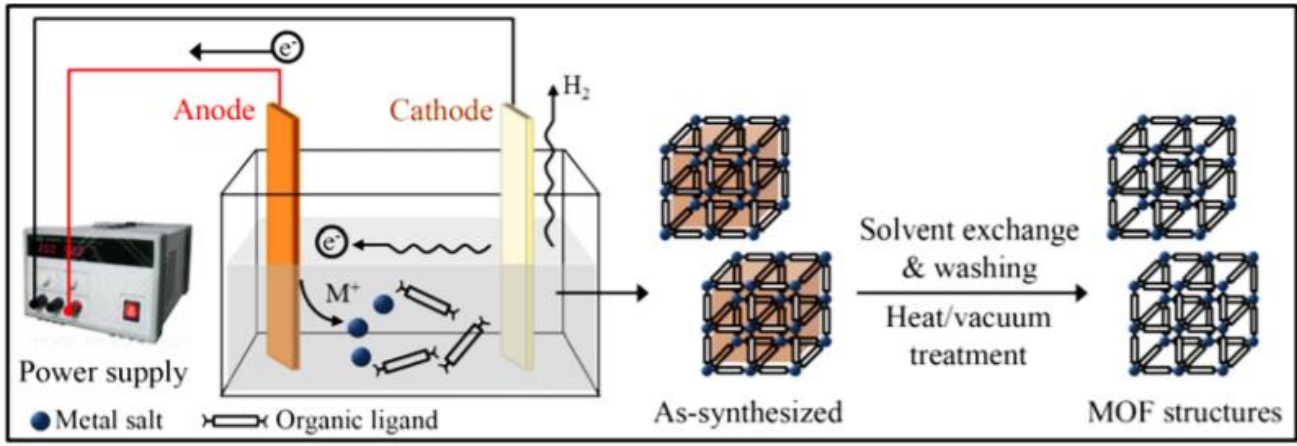


Microwave or sonochemical as alternative heating

Mechanochemistry



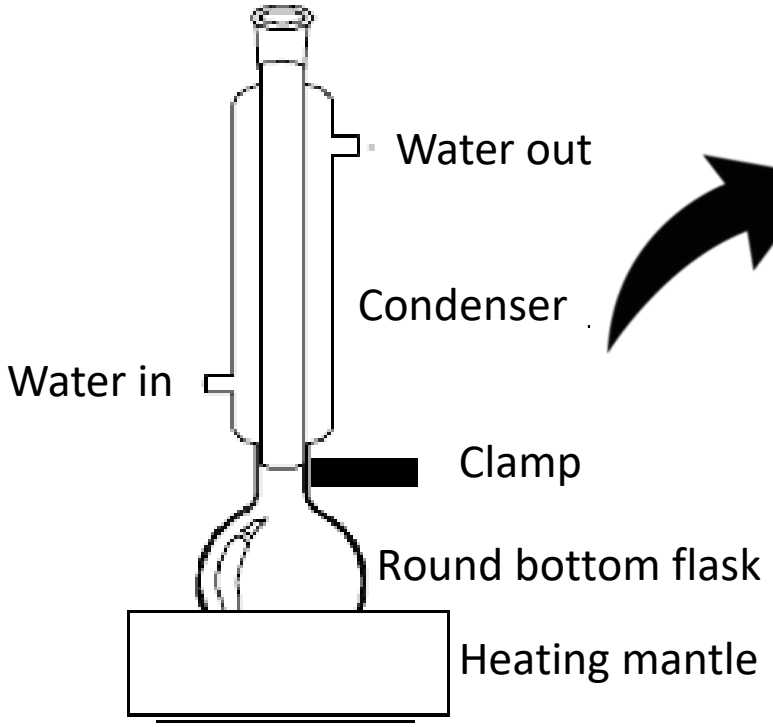
Electrochemistry



*Korean J. Chem. Eng., 30(9), 1667-1680 (2013)

Ambient pressure

- Linker
- Metal
- Solvent
- Modulator



Optimisation

Scale-up

Laboratory scale (mg à g)

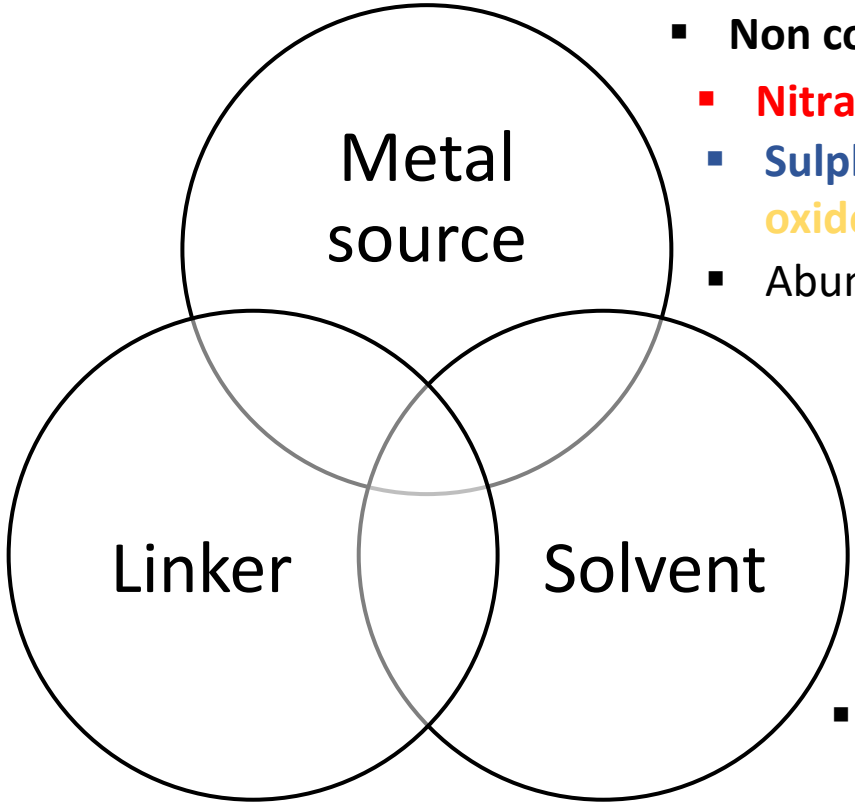
Kilo-pilot-scale (100 g à kg)

Industrial scale (> Ton)

M. Jacoby, Chem. Eng. News, 2013, 91, 34–35

Green synthesis

Low energy



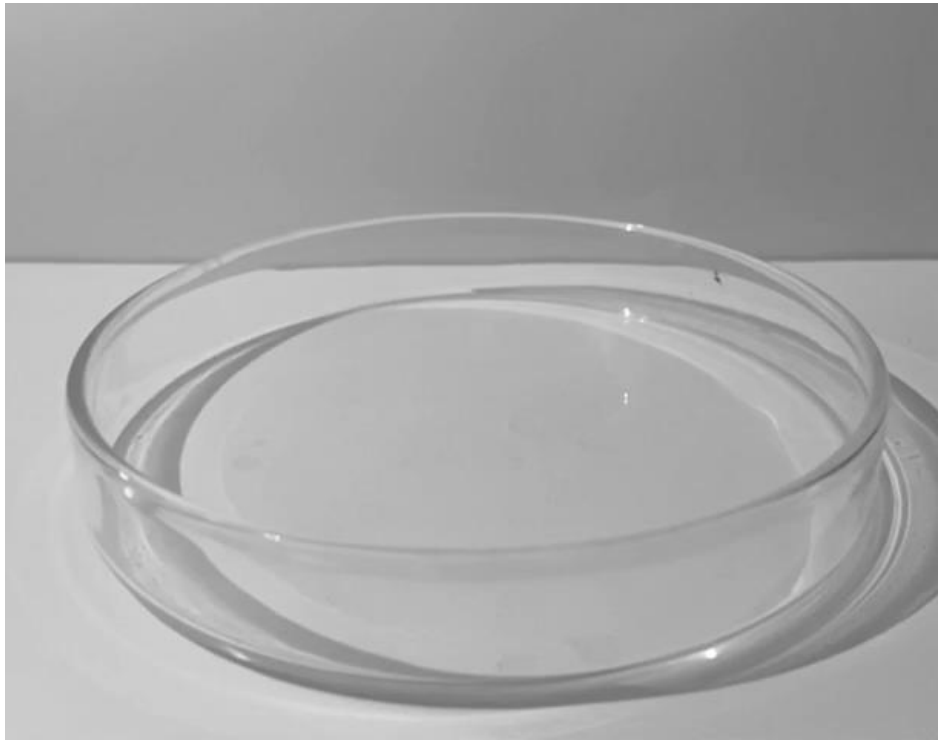
- **Non corrosive**
  - **Nitrate, chloride**
  - **Sulphates, carbonates and oxides (solubility)**
  - Abundant

No toxic by-products

- Non-toxic
- Bio-based
- Abundant

- Inhalation Toxicity
- Carcinogenicity
- Biodegradation

Shaping



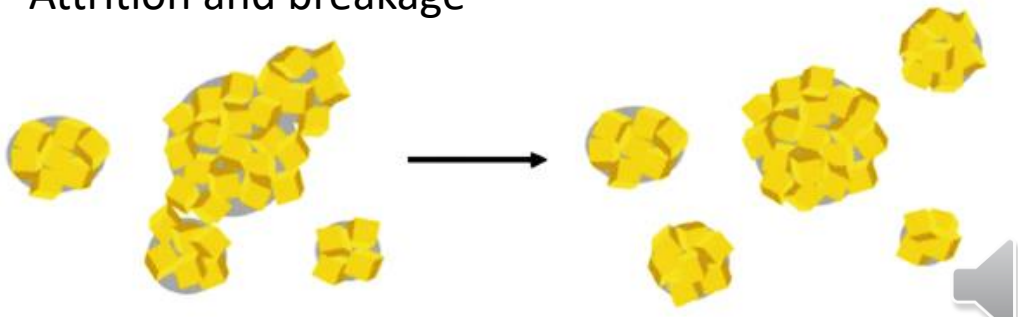
- **Granulation**
- **Extrusion**
- Pelletization
- Foam incorporation
- Monoliths
- Coating

Granulation

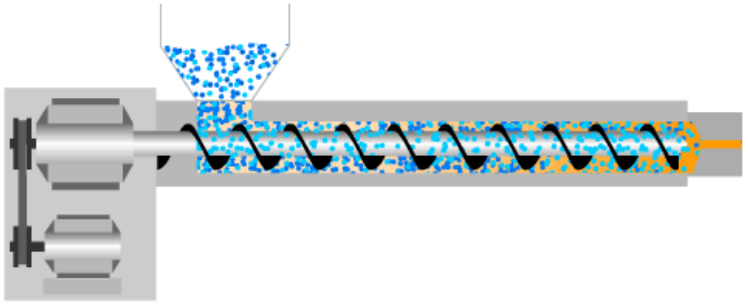
Wetting and nucleation

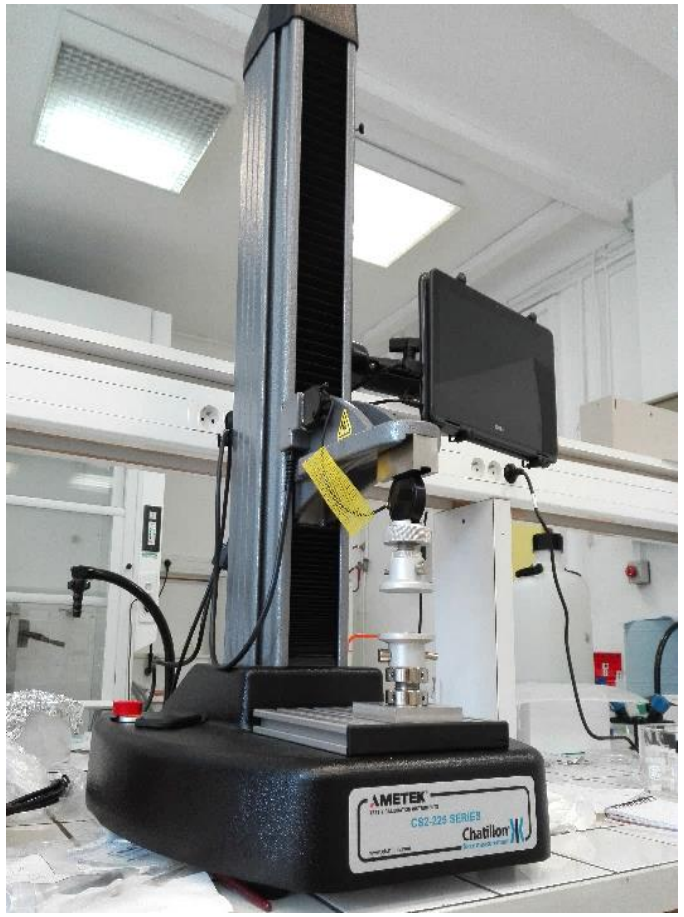
Consolidation and coalescence

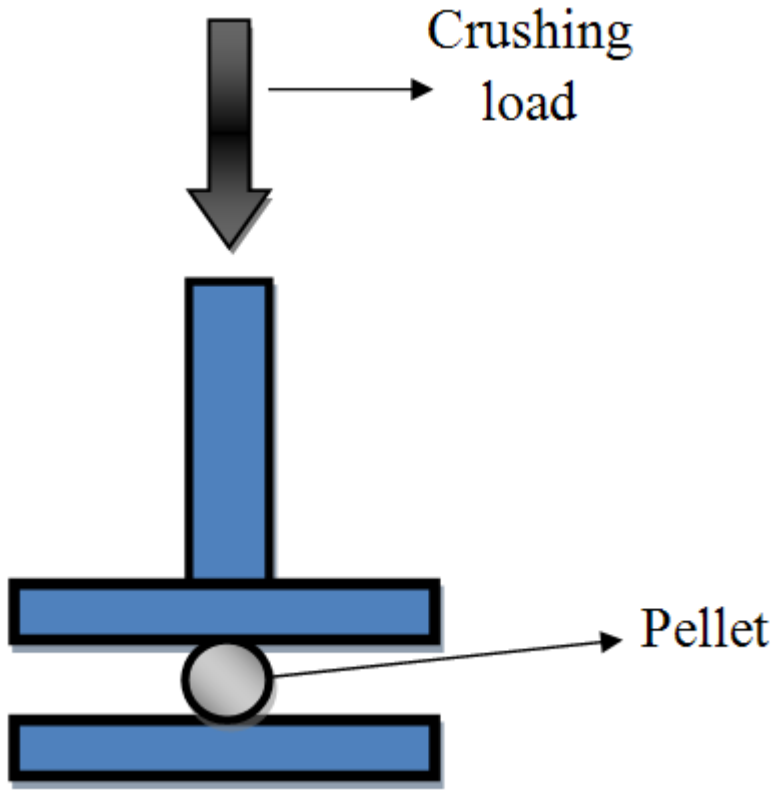
Attrition and breakage



Extrusion







- Stable particles required for application;
- Lower losses of material
- Lower contamination

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Metal-Organic Frameworks as performant adsorbents for cultural heritage preservation

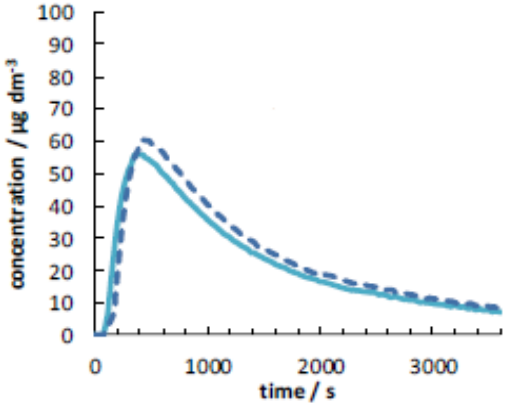
Part II: *Advance characterisation of MOFs materials*

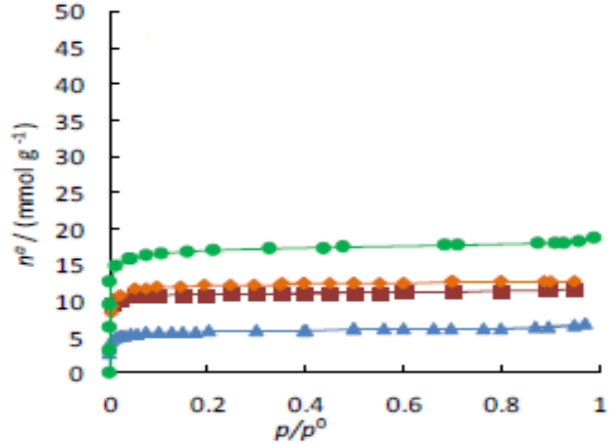
Cátia Freitas IST-ULisboa
catia.freitas@tecnico.ulisboa.pt

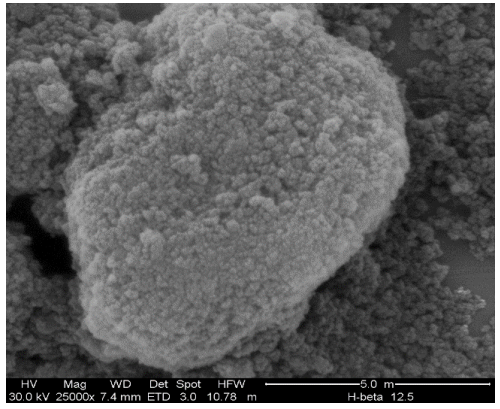
GA760801 funded by

Advance characterisation of Metal-Organic Frameworks

X-ray diffraction
Neutron diffraction
MAS NMR
FTIR
SEM and TEM
Adsorption studies
Computational methods

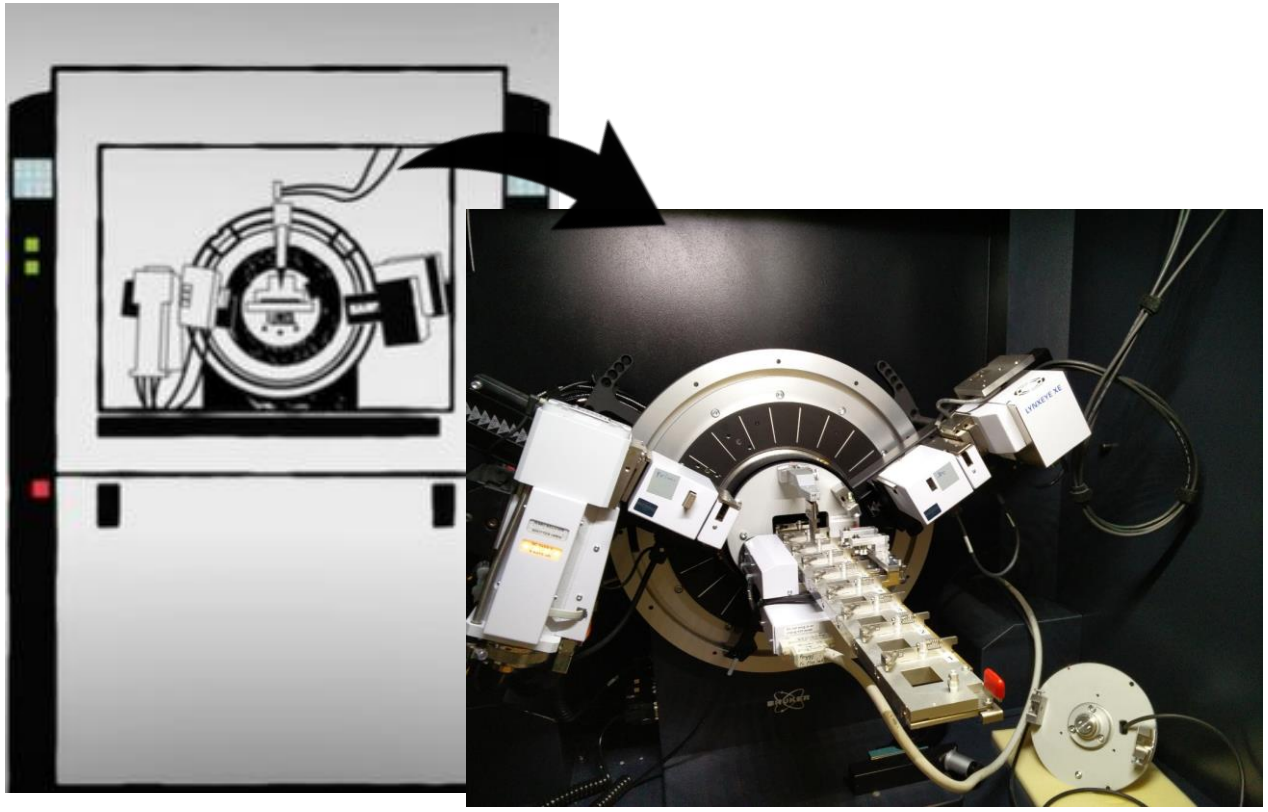


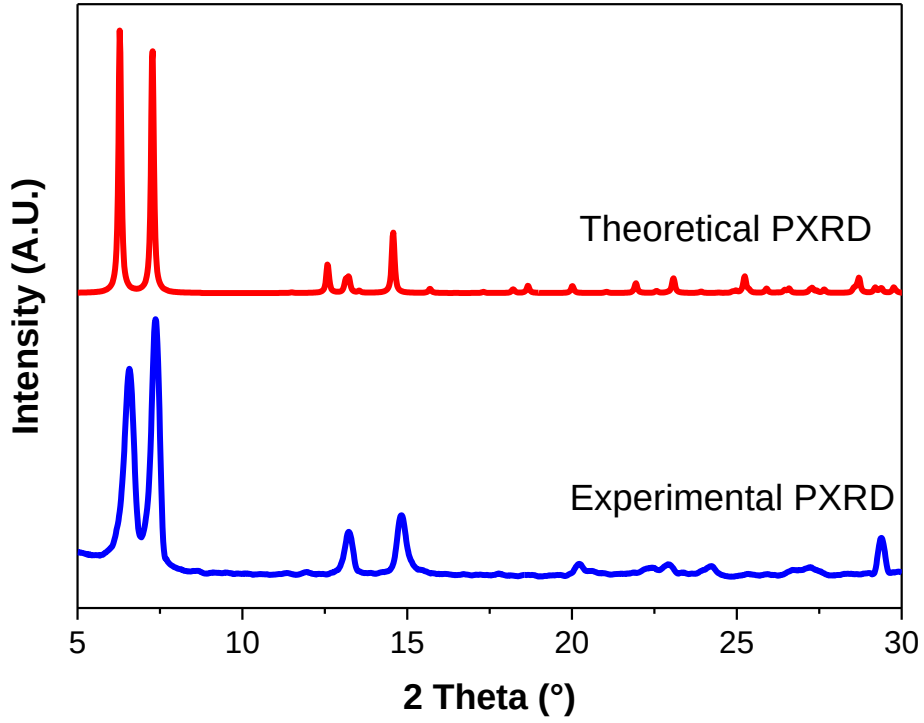




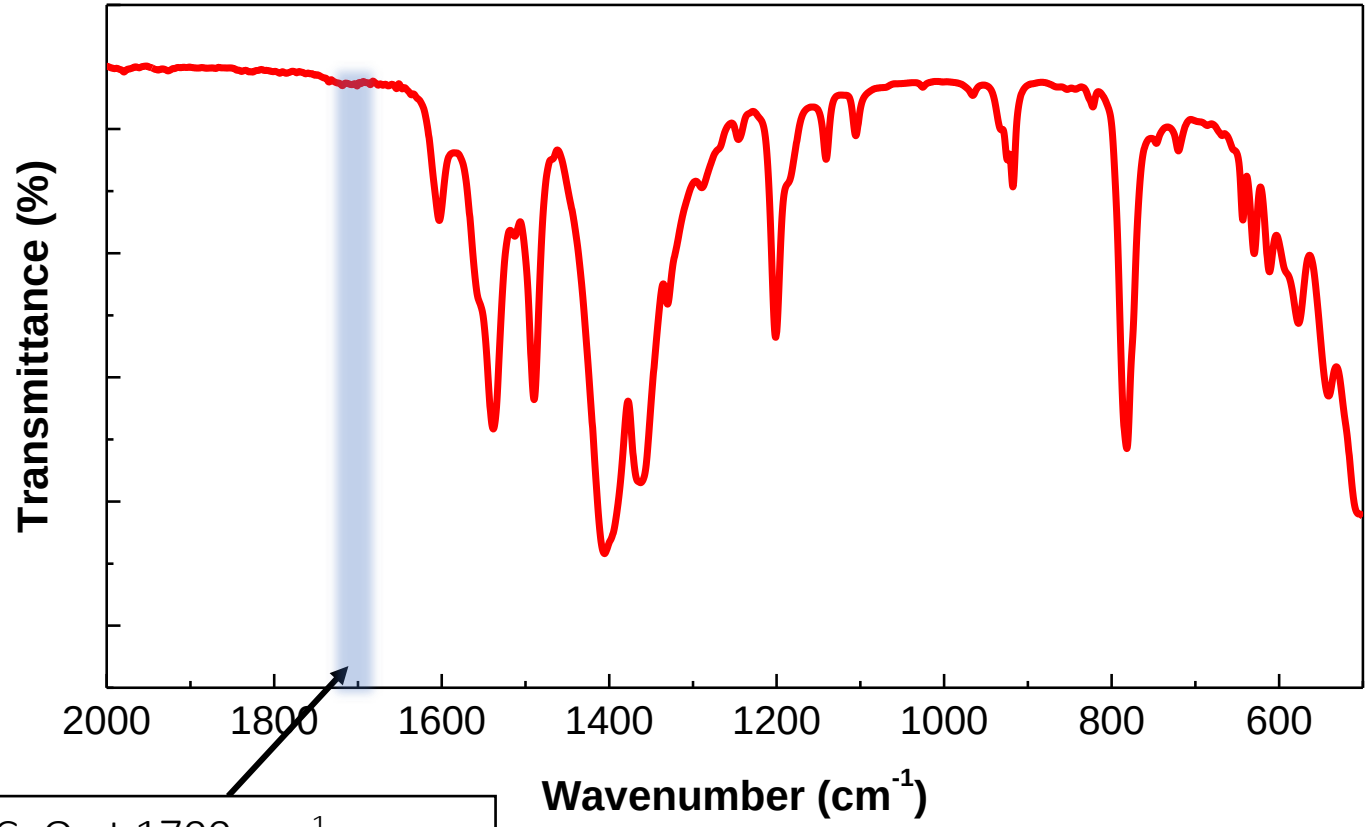
Powder X-ray diffraction (XRD)

- Provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects





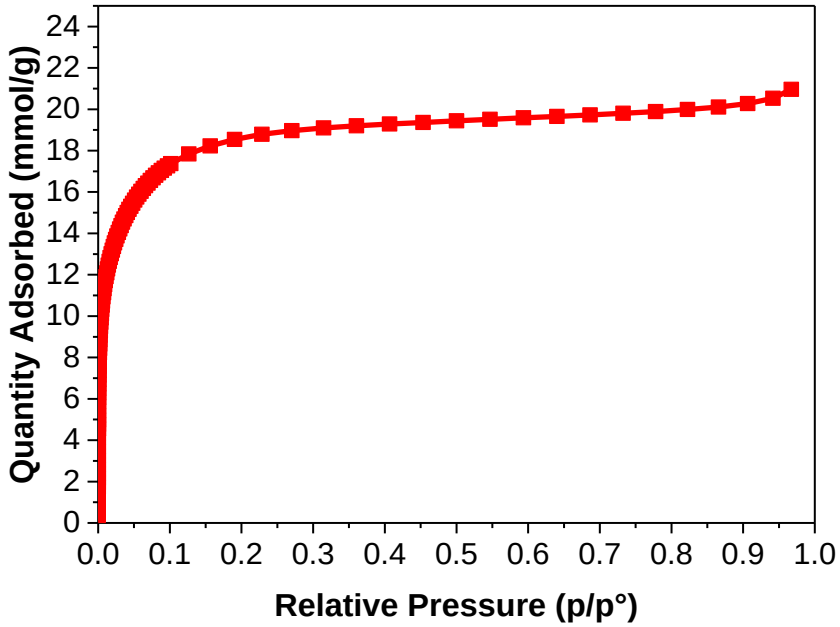
Fourier-transform infrared spectroscopy (FTIR)



No traces of free unreacted linker → νC=O at 1700 cm^{-1}

Nitrogen physisorption

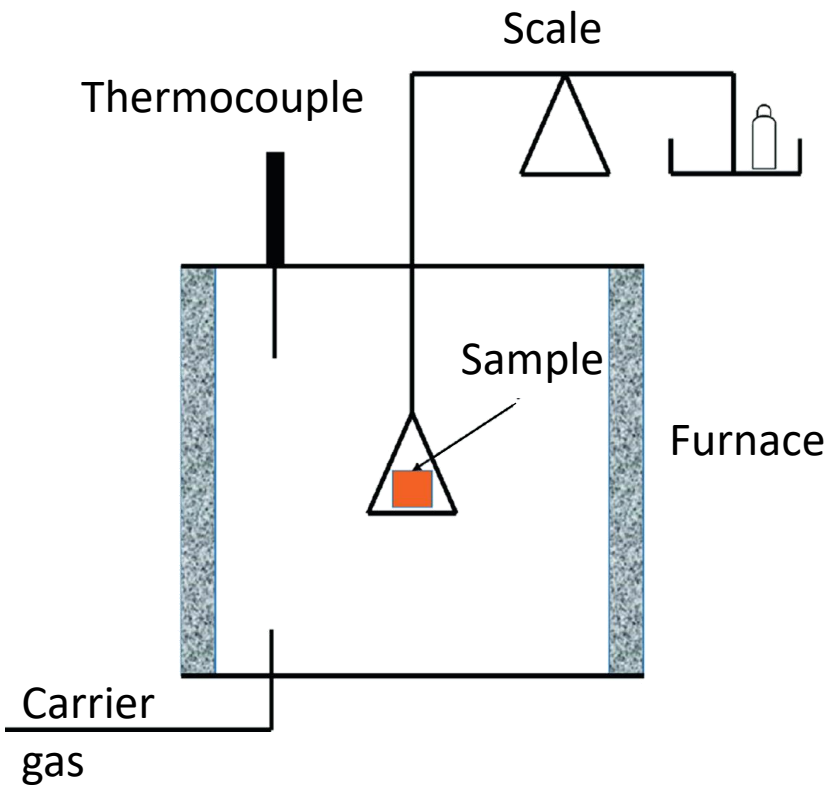
- Gas adsorption off the porous material by measuring the amount of physically adsorbed gas

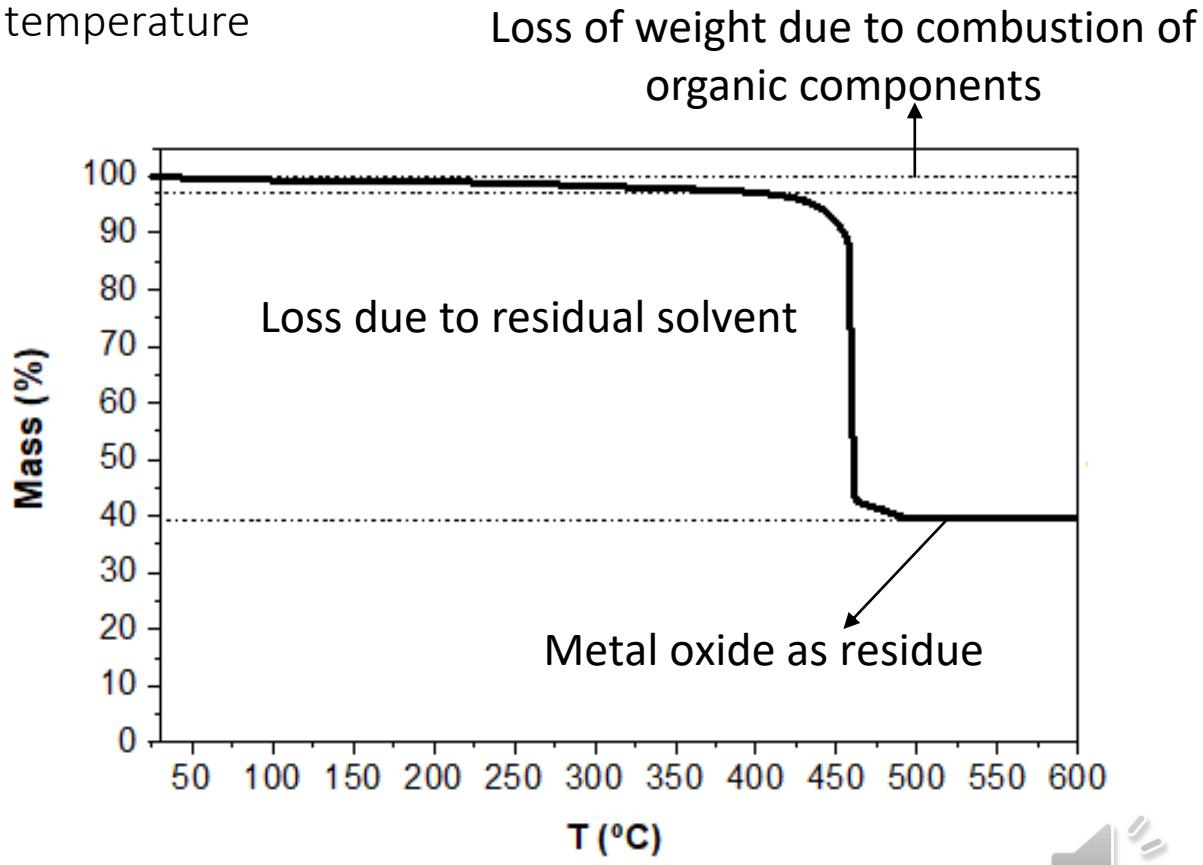


Allows the assessment of microporosity, mesoporosity and surface areas

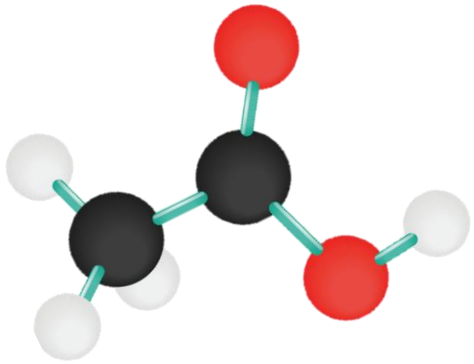
Thermogravimetric analysis (TGA)

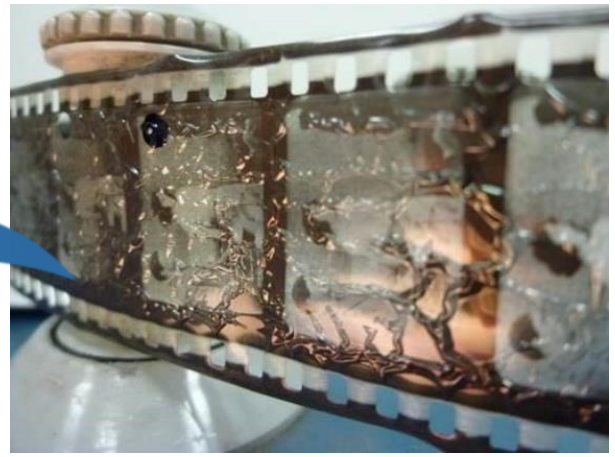
- Method of thermal analysis in which changes in physical and chemical properties of materials are being observed as a result of increase in temperature





Vinegar Syndrome





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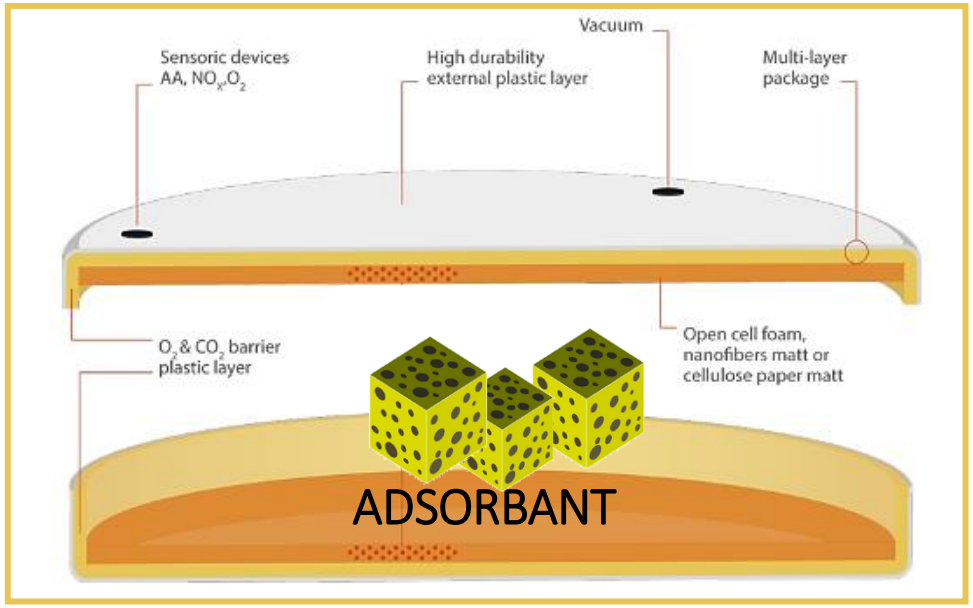
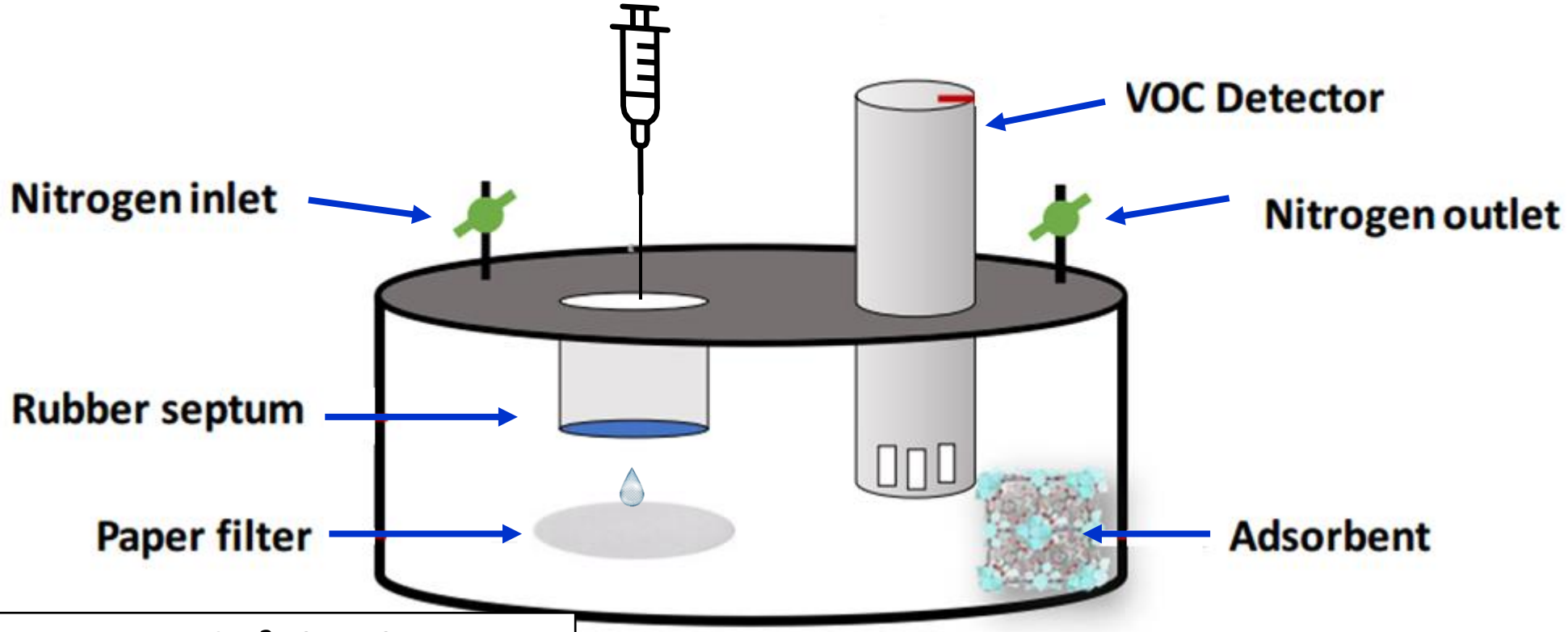


Acetic acid adsorption under controlled moisture level

- Screening test to understand adsorption behaviour



Injection 1 µL in 2.9 dm³ chamber
Relative humidity ~ 40-60 %
Temperature = 25° C

Acetic acid adsorption under controlled moisture level

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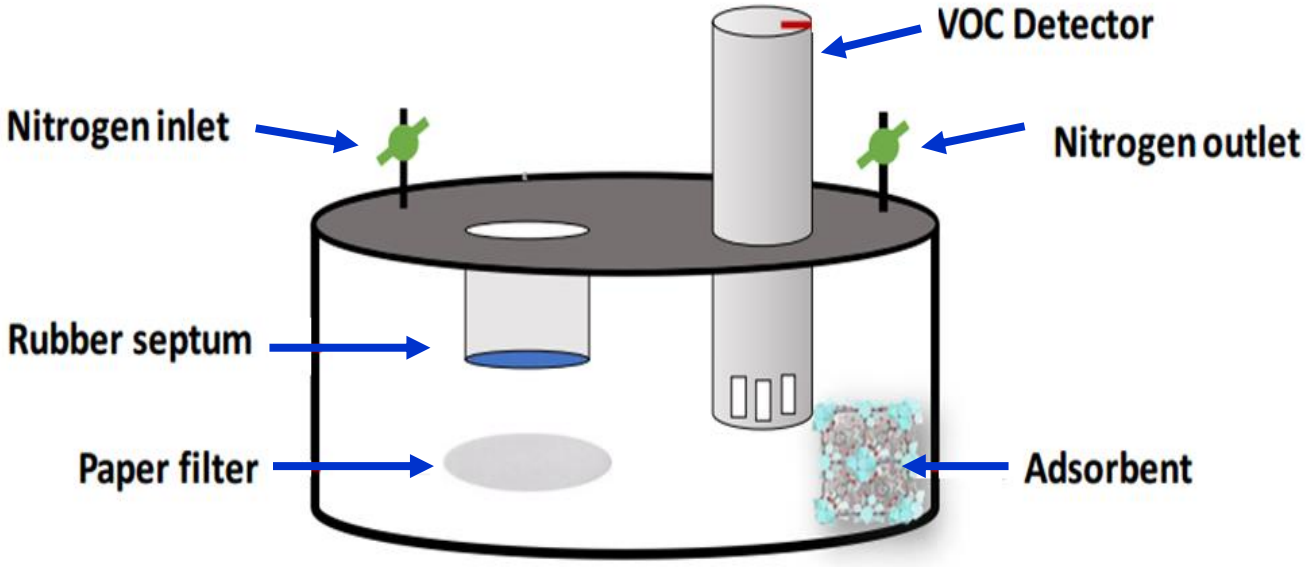
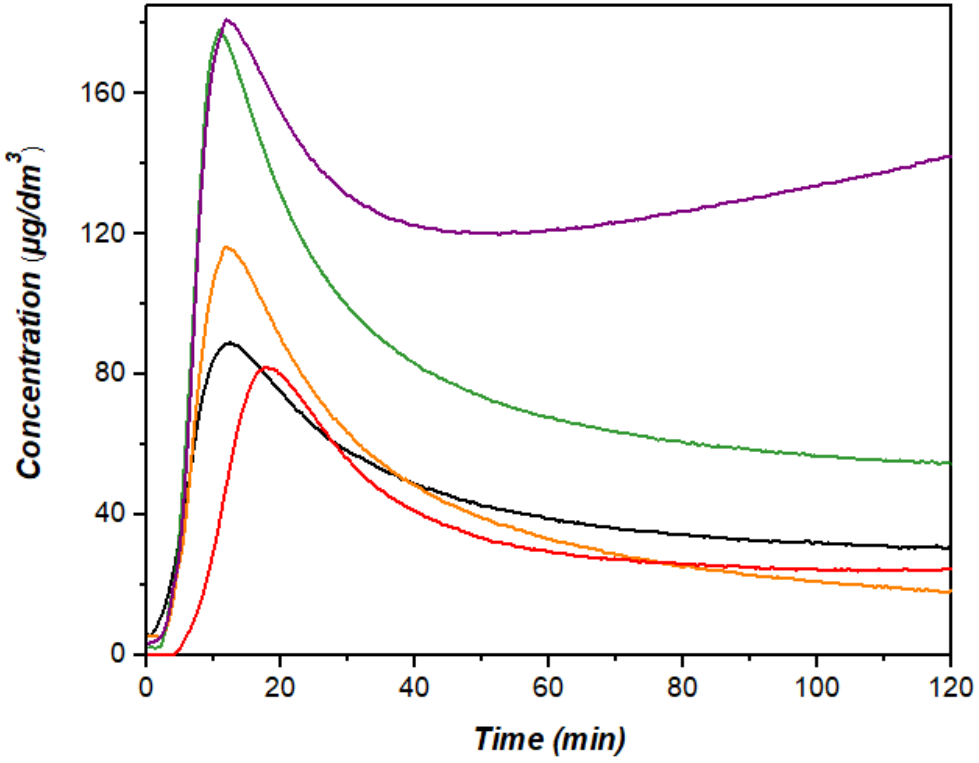
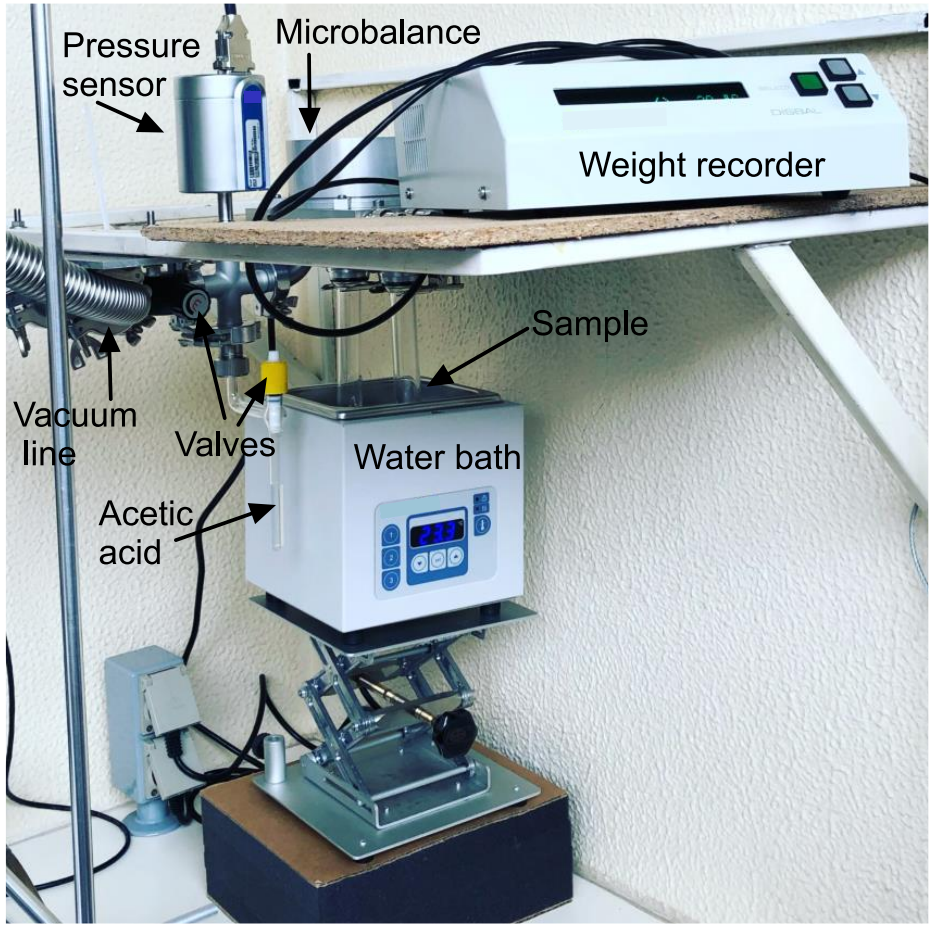
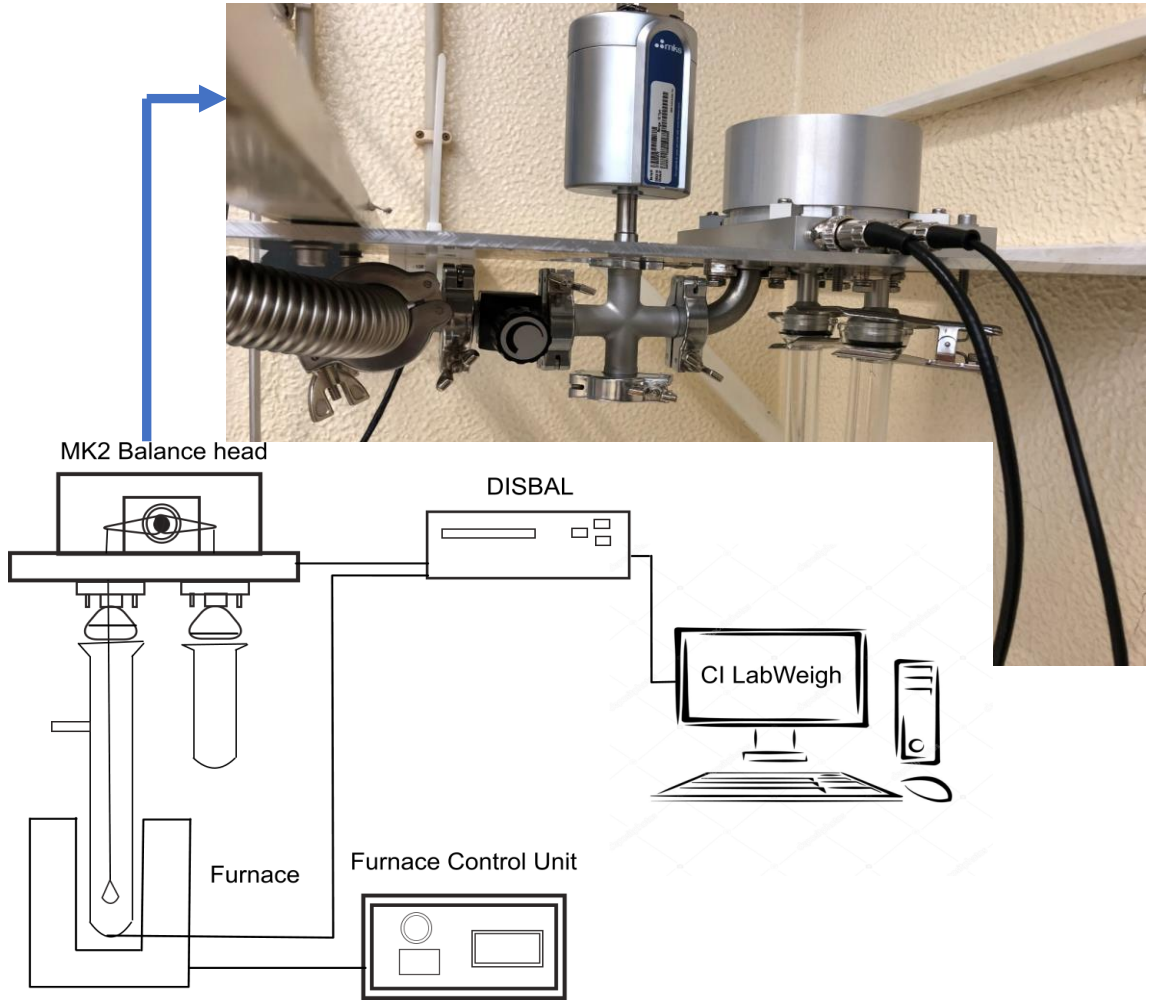




Single component adsorption isotherms





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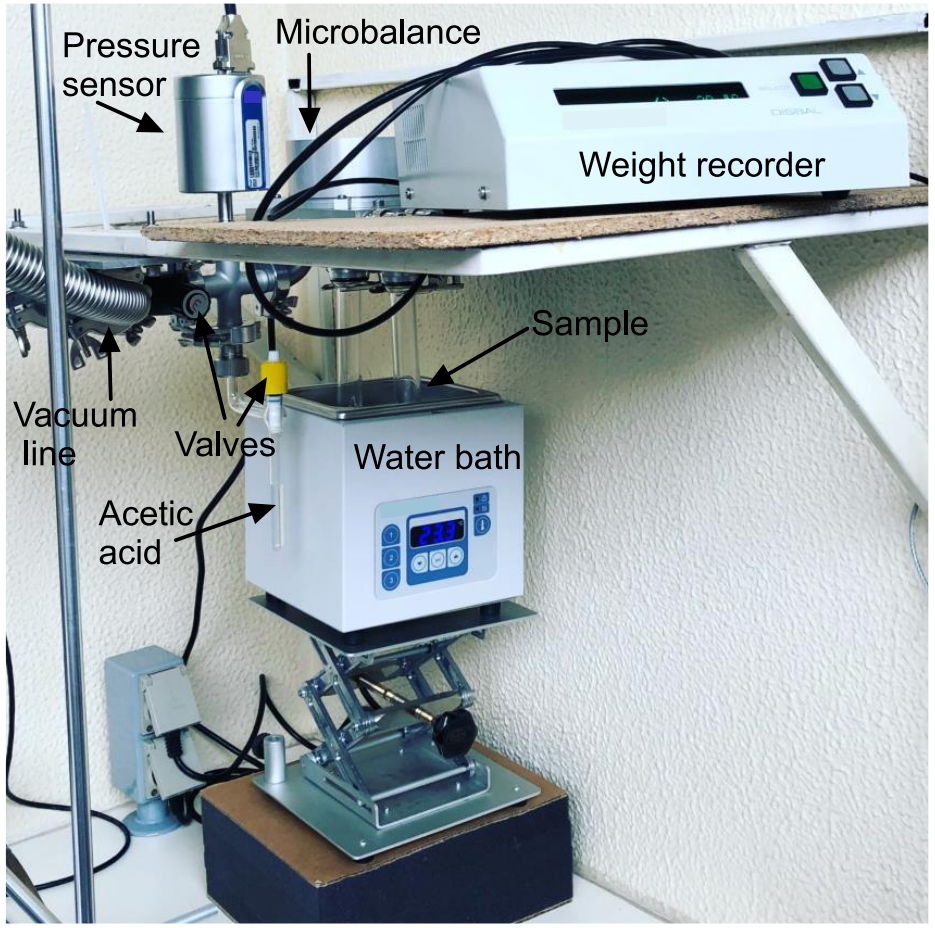
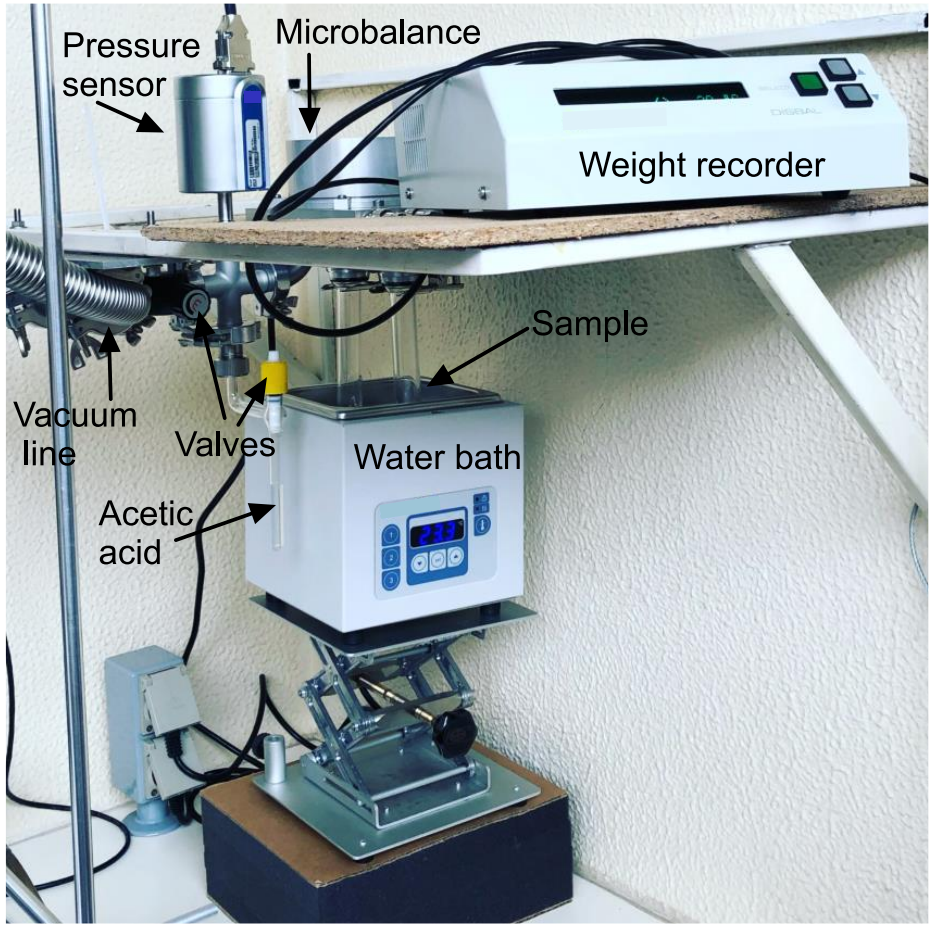
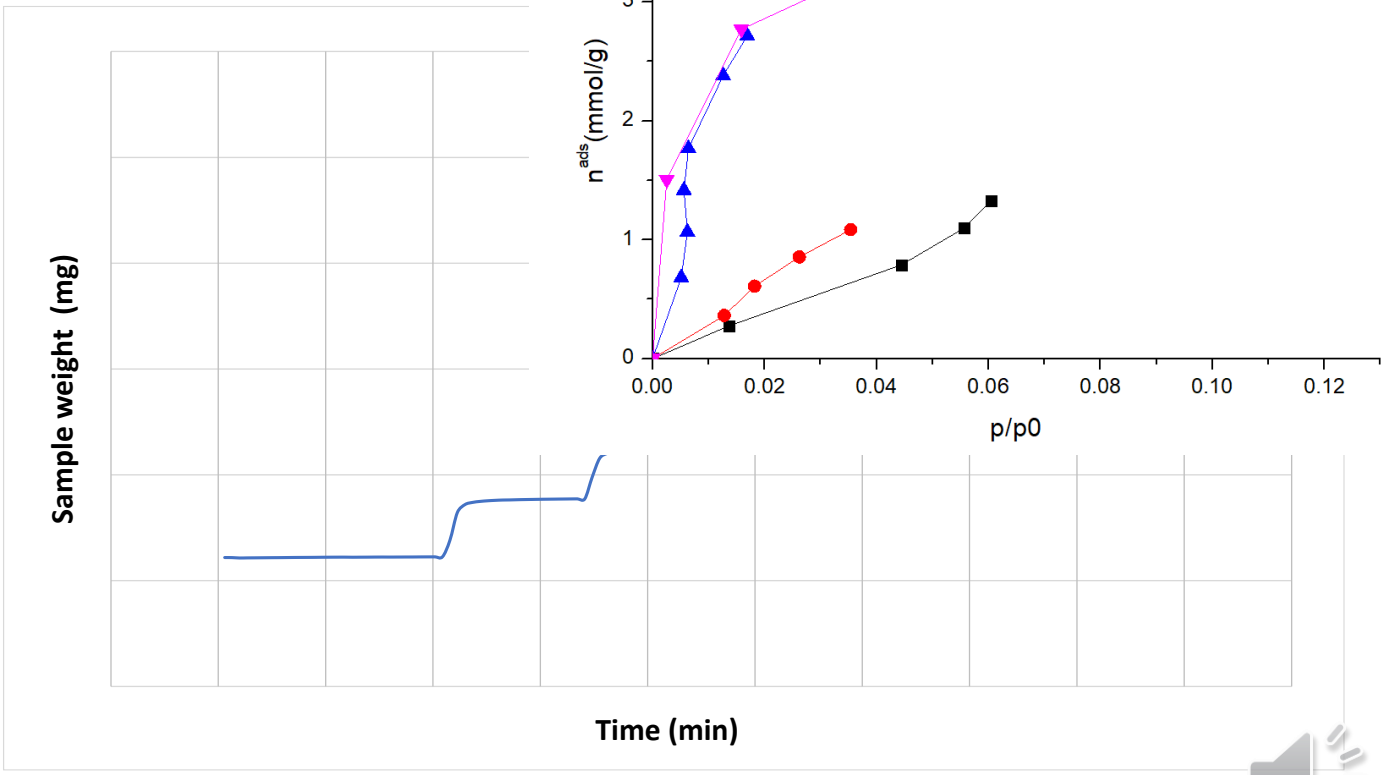


- Measurements are performed **under controlled temperature** and **pressure conditions**
- To access the material **acetic acid capacities** and study their **hydrophobicity**
- More recently: study of adsorption of **other volatile organic compounds** resealed by the decomposition of cellulose acetate materials

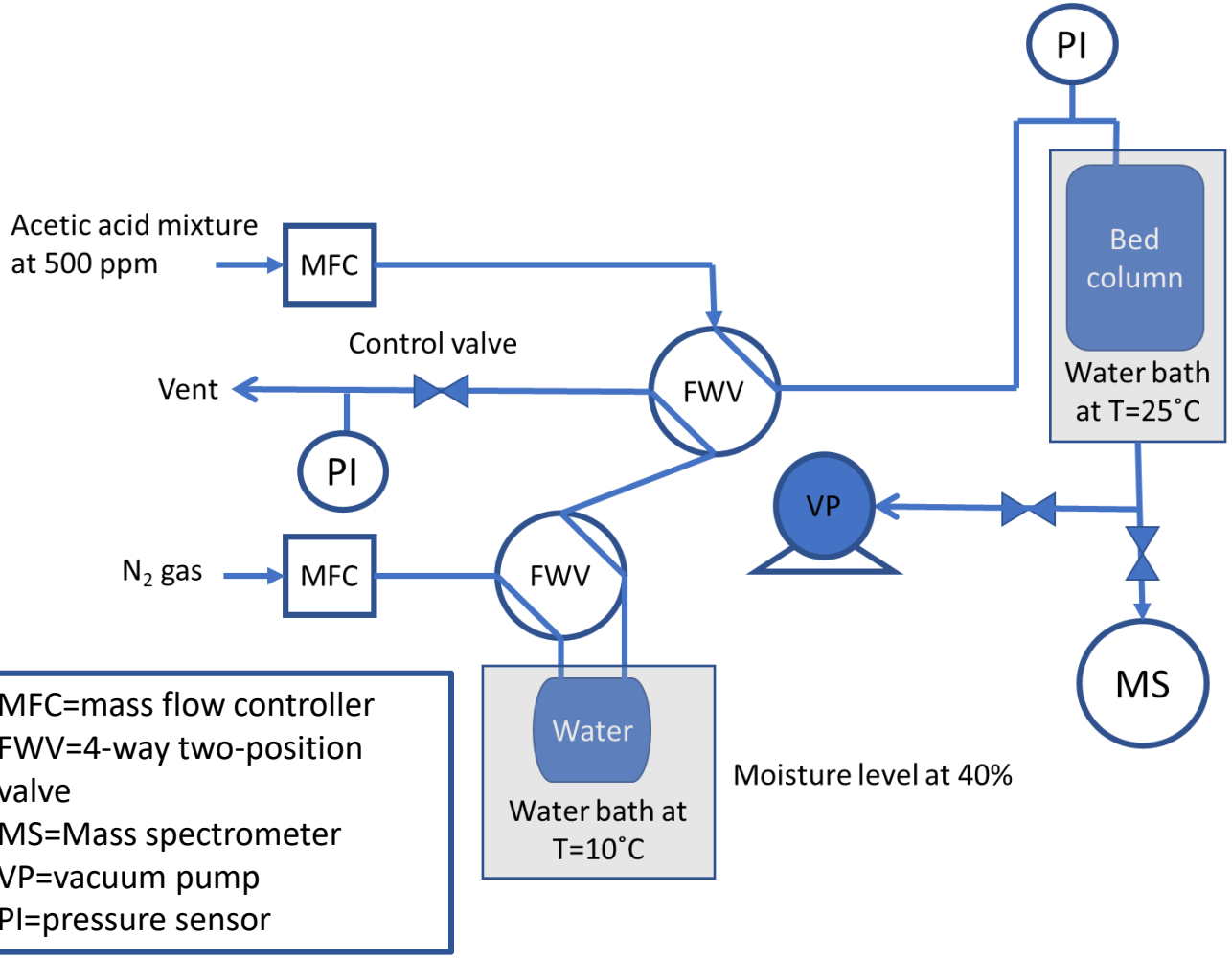
Single component adsorption isotherms





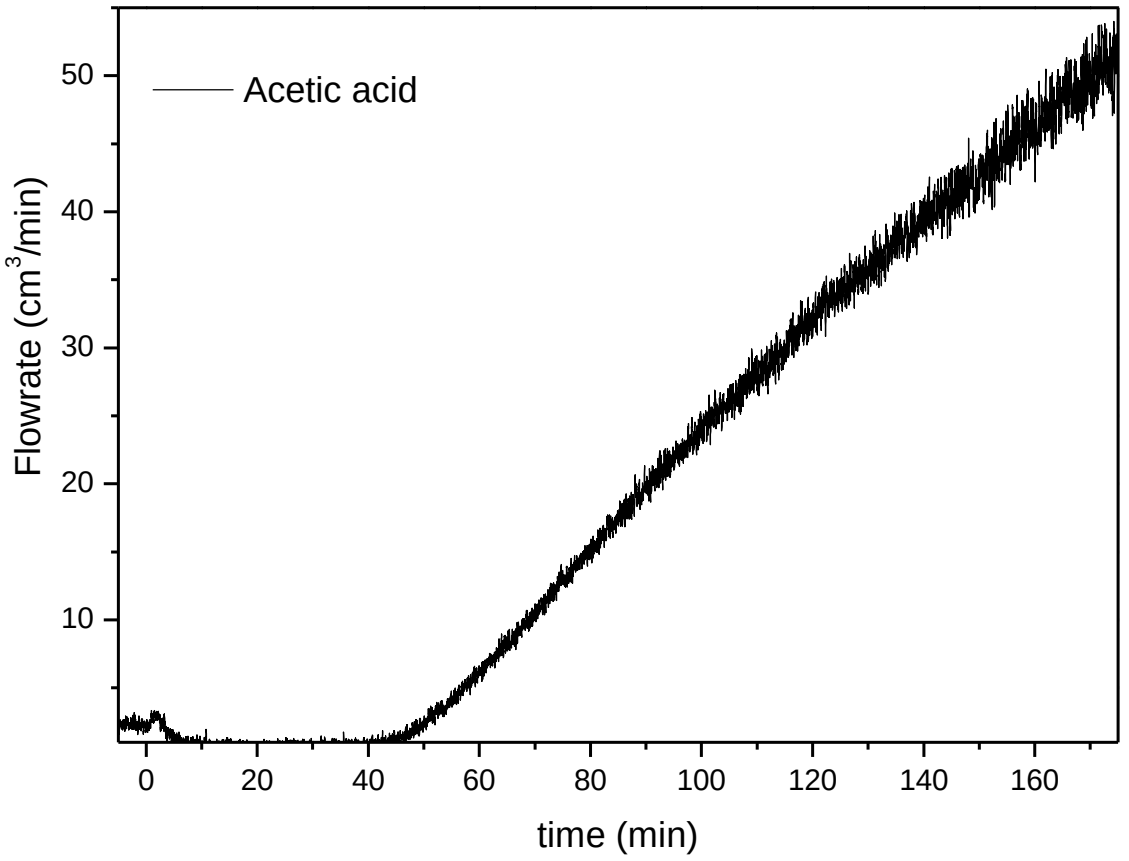
Dedecker, Kevin, et al. "Metal-Organic Frameworks for Cultural Heritage preservation: the case of acetic acid removal." ACS applied materials & interfaces 10.16 (2018)

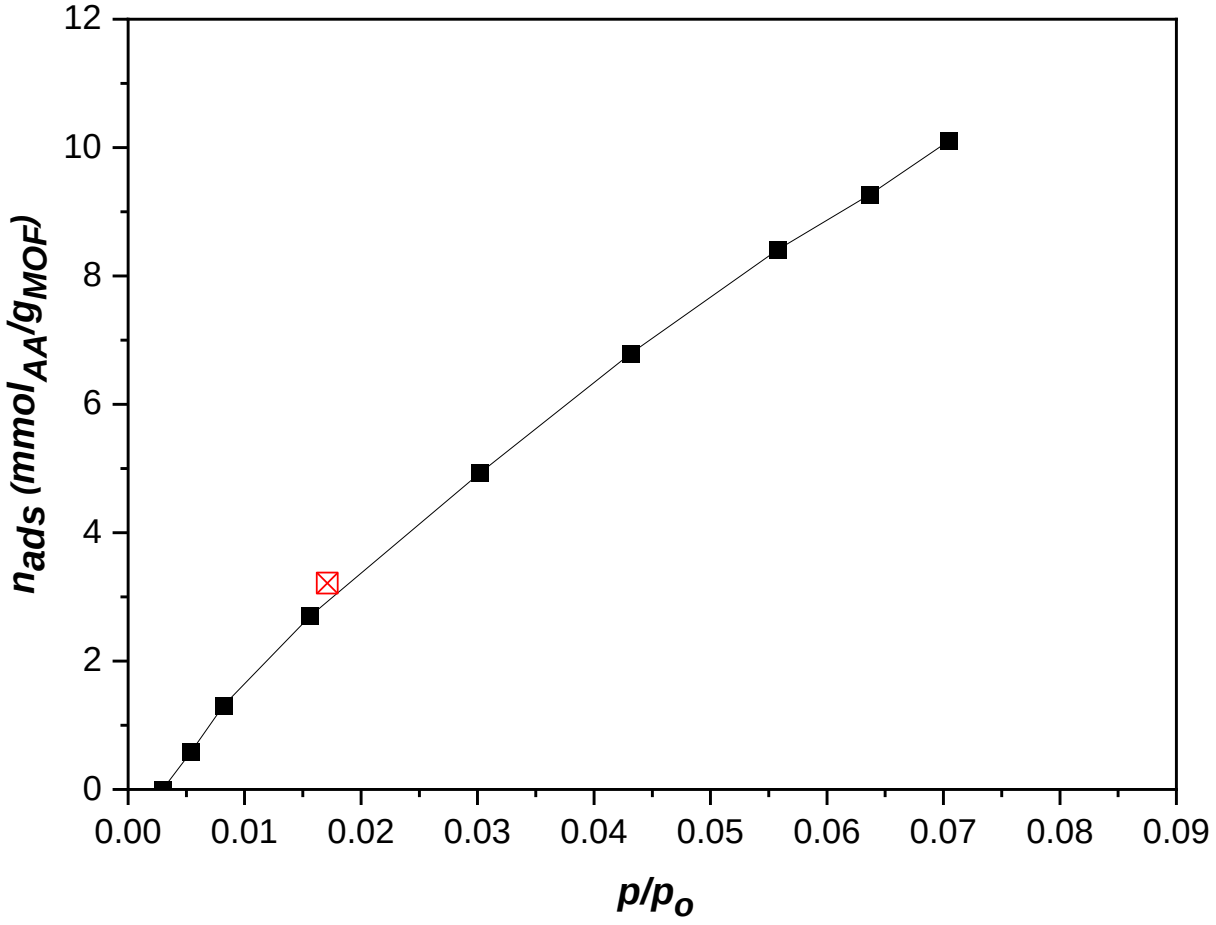
Mass spectrometer setup with multiple gas inlets



MFC=mass flow controller
FWV=4-way two-position valve
MS=Mass spectrometer
VP=vacuum pump
PI=pressure sensor

Mass spectrometer setup with multiple gas inlets





- The adsorbed amount using breakthrough experiment is in perfect agreement with the single component isotherm results.
- This gives us confidence about the performance of the selected material under moisture (in real life application).

Thank you for you attention

catia.freitas@tecnico.ulisboa.pt
maria-ines.severino-neves@espci.fr

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