TRAINING SESSIONS

28th October 2021

NEMOSINE

Innovative packaging solutions for storage and conservation of 20th century cultural heritage of artefacts based on cellulose derivative

HIGH O_2 BARRIER AND ACTIVE PACKAGING

ACTIVE ACID ADSORBERS

MULTI-SCALE MODELLING

GAS DETECTION SENSORS

PACKAGING WITH MODULAR DESIGN

CURATIVE PACKAGES

NEMOSINE has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760801.

Development of Open Cell foams for efficient gases adsorption

Adolfo Benedito

AIMPLAS

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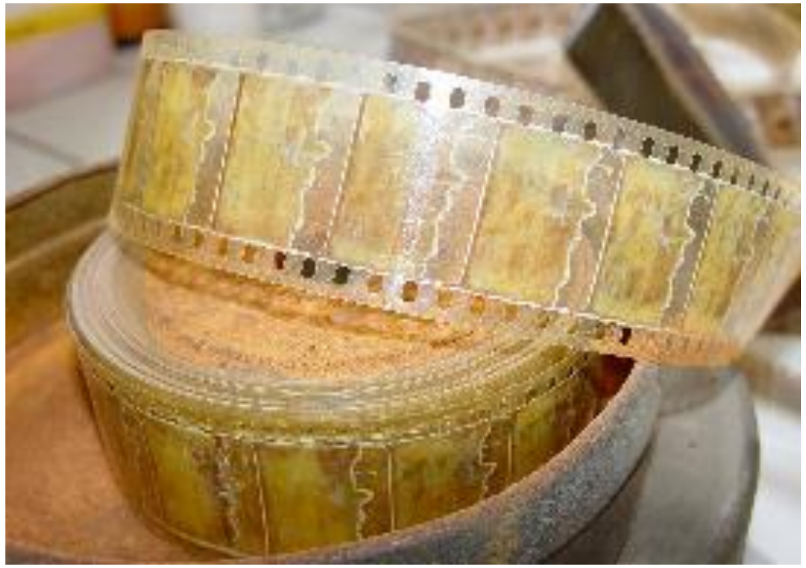
THE NEED

- **The context:**
  - A huge percentage of the recent European cultural heritage (CH) can be found in movies, photographs, posters and slides produced between 1895 to nowadays were made using cellulose derivatives.
  - The worldwide estimation of such holdings within professional film archives is around 18 Mio of film reels on cellulose acetate, whereof ca. 5% are in a critical stage or showing signs of *vinegar syndrome*.



AIMPLAS PLASTICS TECHNOLOGY CENTRE

VINEGAR SYNDROME

Acetic acid is released during the initial acetate base deterioration, leading to the characteristic vinegar odor. This signal marks the progression of deterioration and provokes the acceleration of the process.

A critical objective is **the removing of acetic acid in the environment** to avoid chain degradation reactions.

Traditionally active carbon, zeolites or silicas are useful to control acetic acid emissions. NEMOSINE will apply innovative MOF (Metallic Organic Frameworks) as acetic adsorbers to minimize vinegar syndrome.

location or essay	CH_3COOH (mg/m^3)
British Museum, London, cupboard[4,5]	2.745 ± 0.043
British Museum, London, showcases[4]	2.094 ± 0.060
Musical Instrument Museum, Brussels, showcases[6]	0.604
Musical Instrument Museum, Brussels, gallery[6]	0.082
Plantin-Moretus Museum, Antwerp, showcases[6]	3.215
Plantin-Moretus Museum, Antwerp, gallery[6]	0.106
Museums in Glasgow, Edinburgh, London, and Amsterdam, showcases and storage cabinets[7]	1.8[a]
tests with lead objects[2]	105
tests with calcareous materials[8]	1950[a]
tests with calcareous materials[9]	245[a]

Acetic Acid presence in Museums

VINEGAR SYNDROME

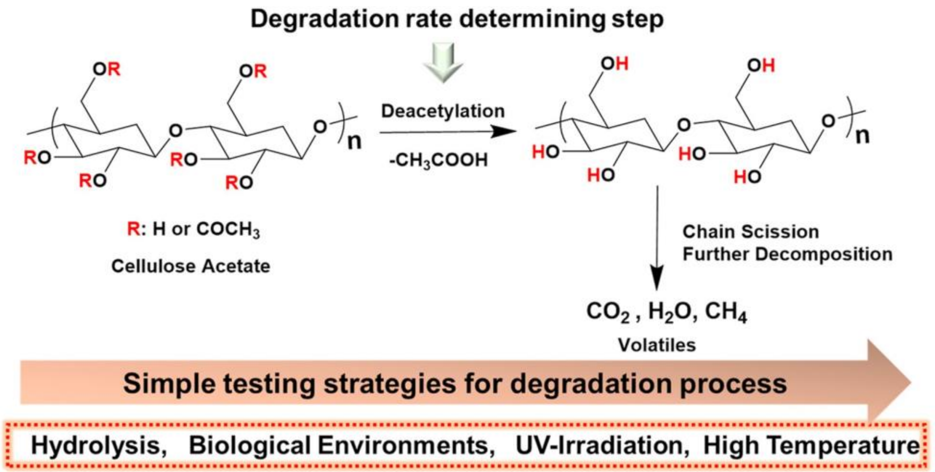
<table>
<tr><th>Film Format</th><th>Film Size</th><th></th><th>1890-1920</th><th>1920</th><th>1925</th><th>1930</th><th>1935</th><th>1940</th><th>1945</th><th>1950</th><th>1955</th><th>1960</th><th>1965</th><th>1965-1980</th><th>1980</th><th>1985-2008</th></tr>
<tr><td rowspan="2">Professional motion picture</td><td rowspan="2">All</td><td>Most Likely</td><td colspan="7">Nitrate</td><td colspan="7">Triacetate</td></tr>
<tr><td>Could Be</td><td colspan="5">Nitrate</td><td colspan="2">Nitrate/Diacetate</td><td>Nitrate</td><td colspan="6">Polyester</td></tr>
<tr><td rowspan="2">Amatuer roll</td><td rowspan="2">35mm</td><td>Most Likely</td><td colspan="4">Nitrate</td><td colspan="3">Diacetate</td><td colspan="6">Triacetate</td><td>Polyester</td></tr>
<tr><td>Could Be</td><td colspan="7">Nitrate</td><td colspan="2">Diacetate</td><td colspan="5">Polyester</td></tr>
<tr><td rowspan="2">Amateur Roll</td><td rowspan="2">120mm</td><td>Most Likely</td><td colspan="7">Nitrate</td><td colspan="6">Triacetate</td><td>Polyester</td></tr>
<tr><td>Could Be</td><td colspan="6">Nitrate</td><td colspan="3">Diacetate</td><td colspan="5">Polyester</td></tr>
<tr><td rowspan="2">Microfilm</td><td rowspan="2">35/16mm</td><td>Most Likely</td><td></td><td colspan="3">Nitrate</td><td colspan="3">Diacetate</td><td colspan="5">Triacetate</td><td colspan="2">Polyester/Triacetate</td></tr>
<tr><td>Could Be</td><td></td><td colspan="6">Nitrate/Diacetate</td><td colspan="2">Diacetate</td><td colspan="5">Polyester/Triacetate</td></tr>
<tr><td rowspan="2">Microfiche</td><td rowspan="2">105mm</td><td>Most Likely</td><td></td><td colspan="3">Nitrate</td><td colspan="3">Diacetate</td><td colspan="5">Triacetate</td><td colspan="2">Polyester</td></tr>
<tr><td>Could Be</td><td></td><td colspan="6">Nitrate/Diacetate</td><td colspan="2">Diacetate</td><td colspan="5">Polyester/Triacetate</td></tr>
<tr><td rowspan="2">Sheet Film</td><td rowspan="2">All</td><td>Most Likely</td><td colspan="4">Nitrate</td><td colspan="3">Diacetate</td><td colspan="5">Triacetate</td><td colspan="2">Polyester</td></tr>
<tr><td>Could Be</td><td colspan="2">Nitrate</td><td colspan="7">Nitrate/Diacetate</td><td colspan="5">Polyester</td></tr>
</table>

VINEGAR SYNDROME

The acetic acid can act as a catalyst (an accelerator that is not consumed) in many hydrolytic reactions (reactions with water). Sensitive materials include typical chromogenic yellow dyes, cellulose acetate and nitrate, gelatin and many other polymeric binders. In addition, acids can aid in making oxidizing agents even more active.

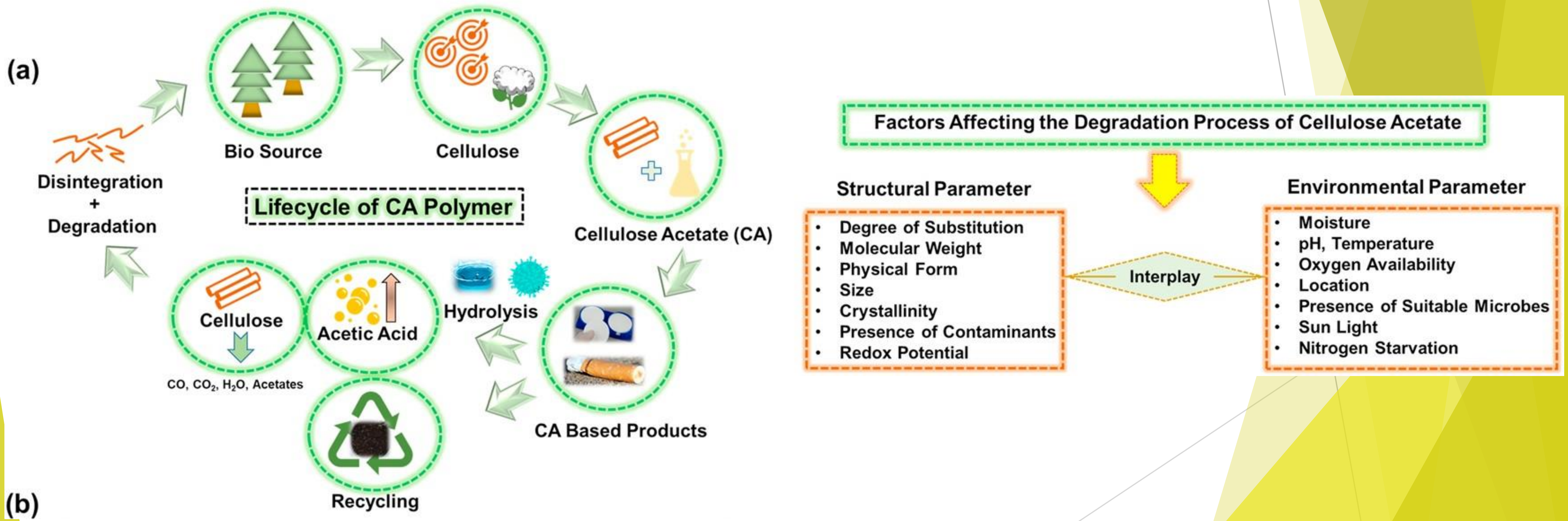
$$[(C_6H_5O_2) - (O - \overset{\overset{O}{\|}}{C} - CH_3)_3]_n \; + \; H_2O \longrightarrow [(C_6H_5O_2) - (O - \overset{\overset{O}{\|}}{C} - CH_3)_2]_n \; + \; CH_3COOH$$

Cellulose Triacetate — Cellulose Diacetate — Acetic Acid



VINEGAR SYNDROME

Proposed lifecycle of Cellulose Acetate polymers and factors:



VINEGAR SYNDROME

- The removal of acetic acid vapors, a degradation byproduct, retards further degradation by reducing the autocatalytic effect and limits the risk of infectious behavior.

- High active surface materials have showed important AA adsorption performance.

sample label	type and origin	form	A_{BET} (m^2/g)	V_{DR} (cm^3/g)	m^{max} (g_{vapor}/g_{sample})	V^{max}/V_{DR} (%)
CarbTech	Carbon Tech	pellet	977	0.41	0.50	117
RB1	carbon RB1, Norit	pellet	985	0.44	0.47	103
RB3	carbon RB3, Norit	pellet	1305	0.53	0.44	80
RB4	carbon RB4, Norit	pellet	1320	0.54	0.54	95
NaX	zeolite 13X, BDH	powder	613	0.26	>1.25	>456
NaX(P)	zeolite 13X, BDH	pellet	533	0.22	>0.77	>335
NaY	zeolite Y, Aldrich	powder	835	0.34	0.48	135
Al-WYO	pillared clay	powder	270	0.10	0.28	264
SG60	silica gel 60	powder	490	(0.72)[b]	0.07	(9)[c]

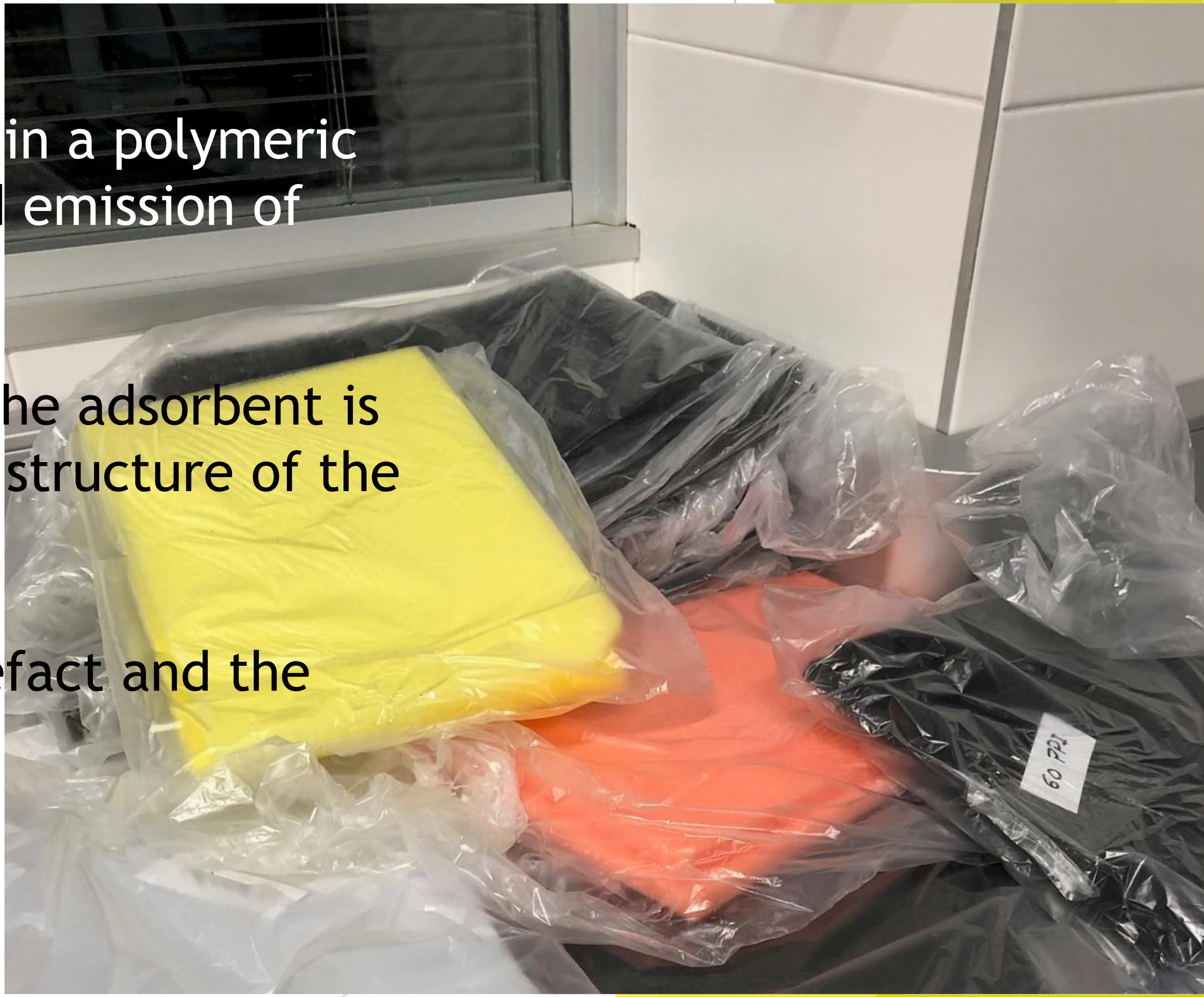
m_{max}, saturation capacity for acetic acid at room temperature;

FOAMS AS SUPPORTING MATERIAL FOR ADSORBENTS

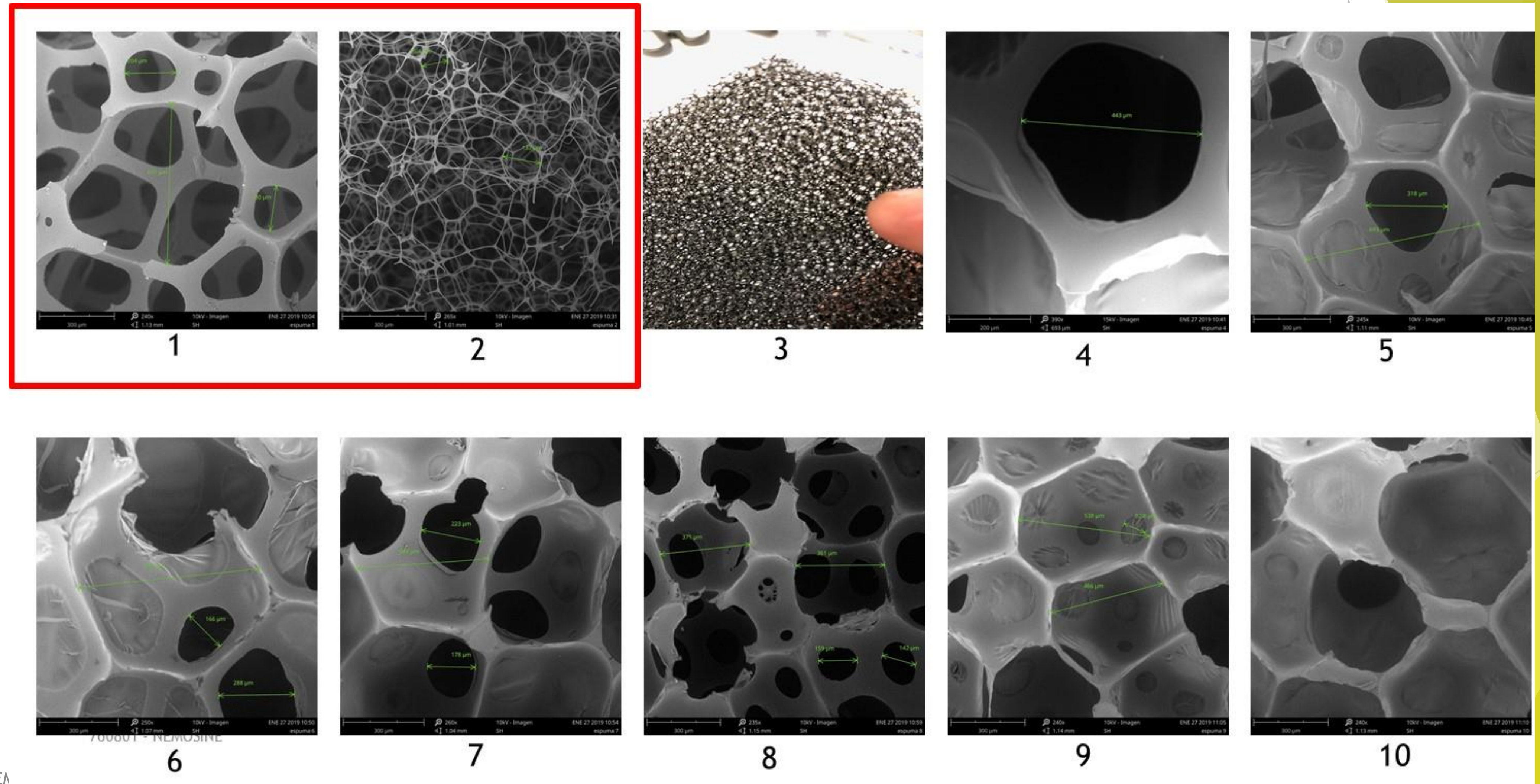
- Adsorbent particles immobilized in a polymeric matrix, such as a foam, can avoid emission of particles to the CH artefacts.

- Accessibility of the AA vapors to the adsorbent is high because of the macroporous structure of the foams.

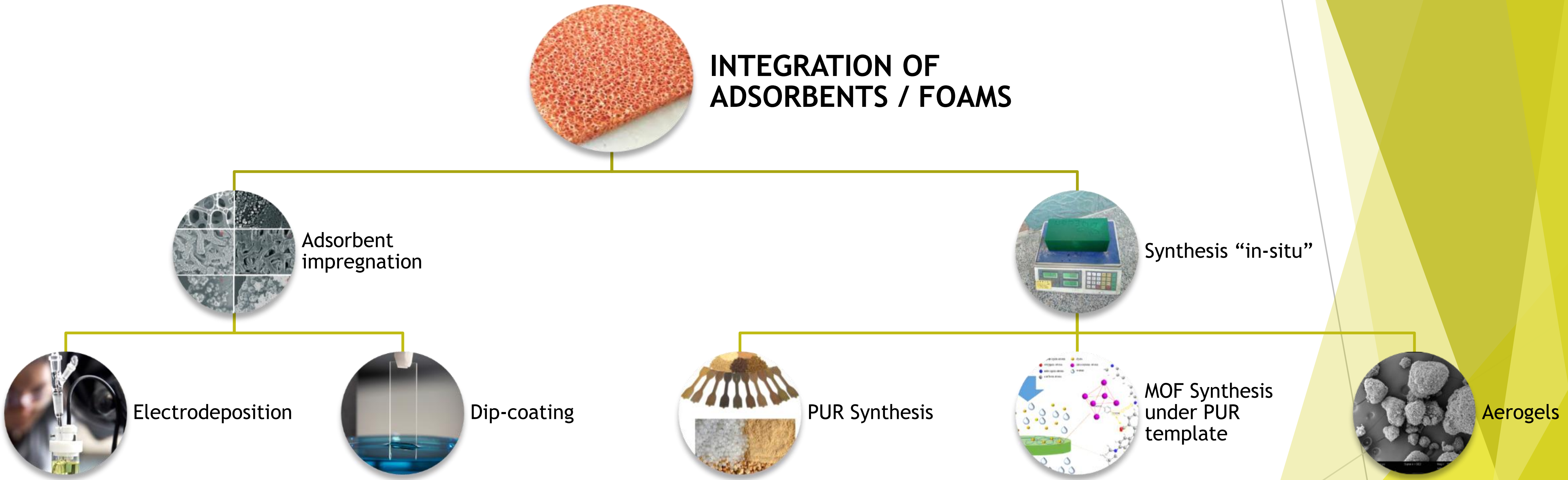
- Mechanical protection to the artefact and the own adsorber.



FOAMS AS SUPPORTING MATERIAL FOR ADSORBENTS



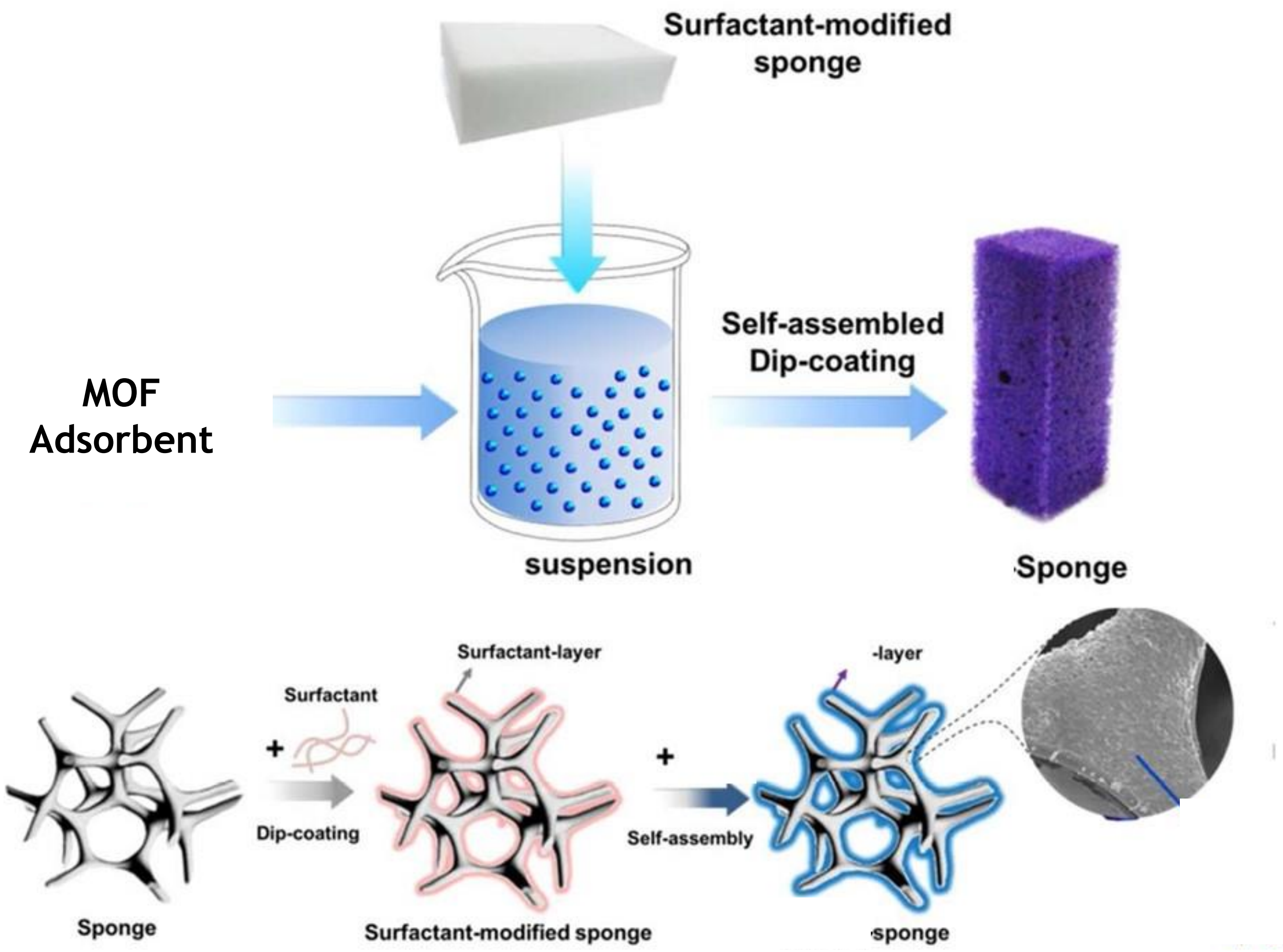
FOAMS AS ADSORBENTS: METHODOLOGIES



FOAMS AS ADSORBENTS: METHODOLOGIES

- **Impregnation Process**
  - Compounding
  - Impregnation
  - Washing
  - Drying
  - Converting
- **Foam “in situ” Process**
  - Mixing
  - Foaming
  - Converting

ADSORBENT IMPREGNATION



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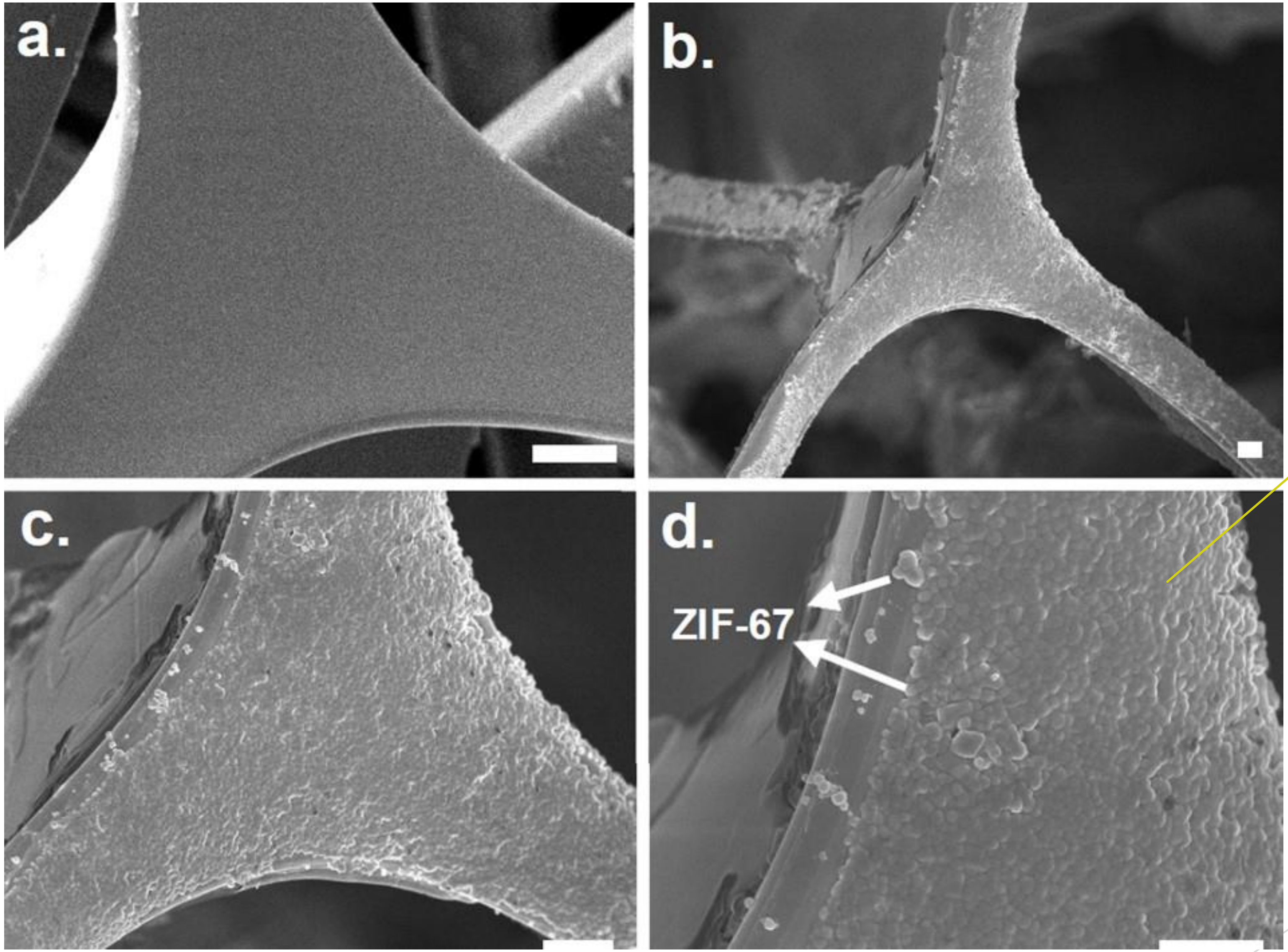
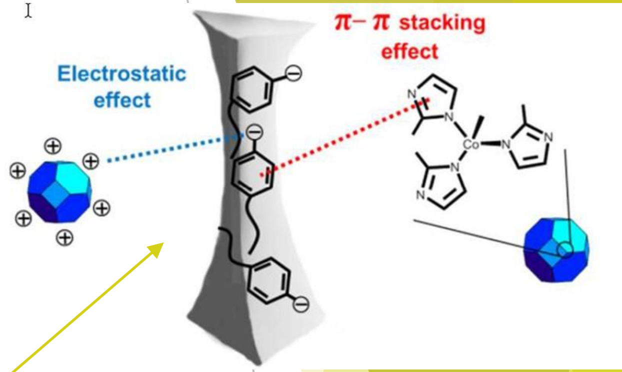


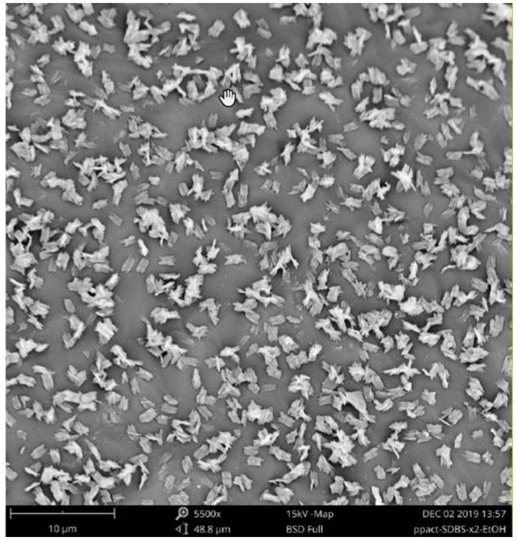


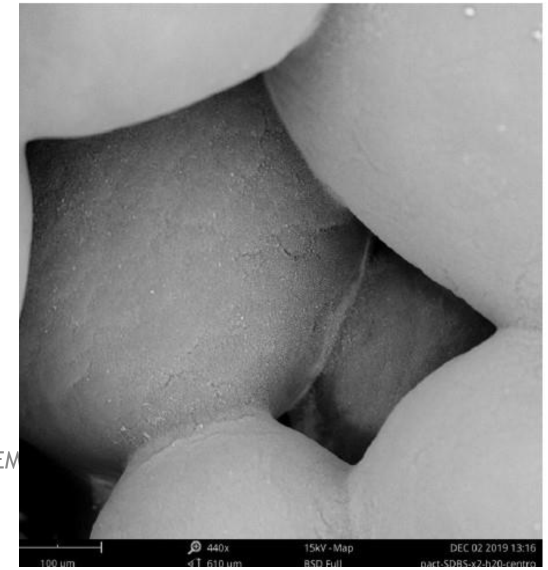
a) Pristine sponge.
b) Surfactant treatment.
c) Impregnated MOFs.
d) Impregnated MOFs.

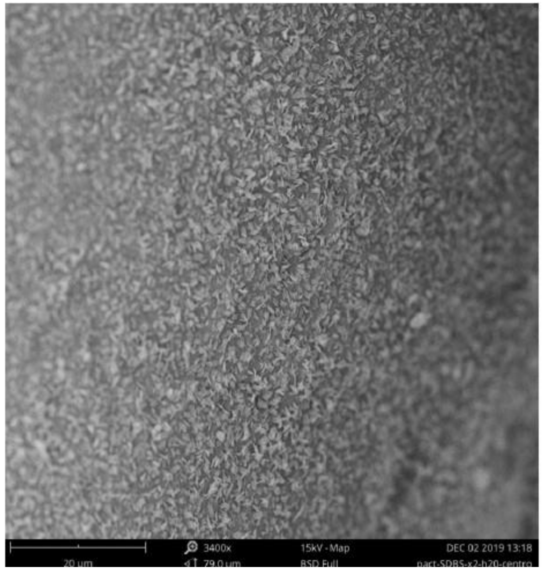
Potential applications: filters, membranes or adsorbents.

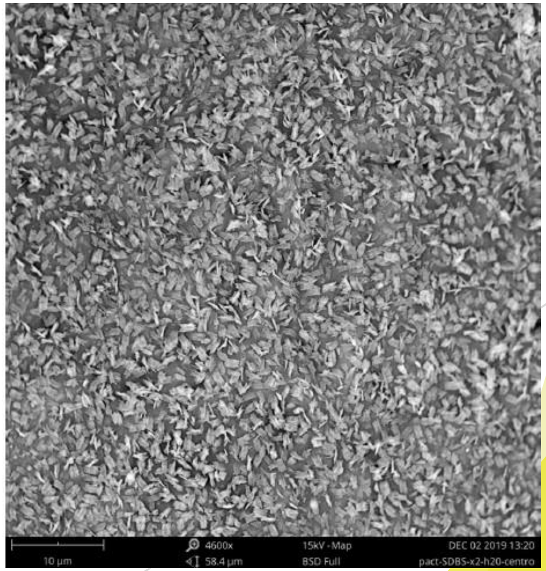
K. A. Lin and H. Chang, *J. Mater. Chem. A*, 2015, DOI: 10.1039/C5TA04427H.

ADSORBENT IMPREGNATION









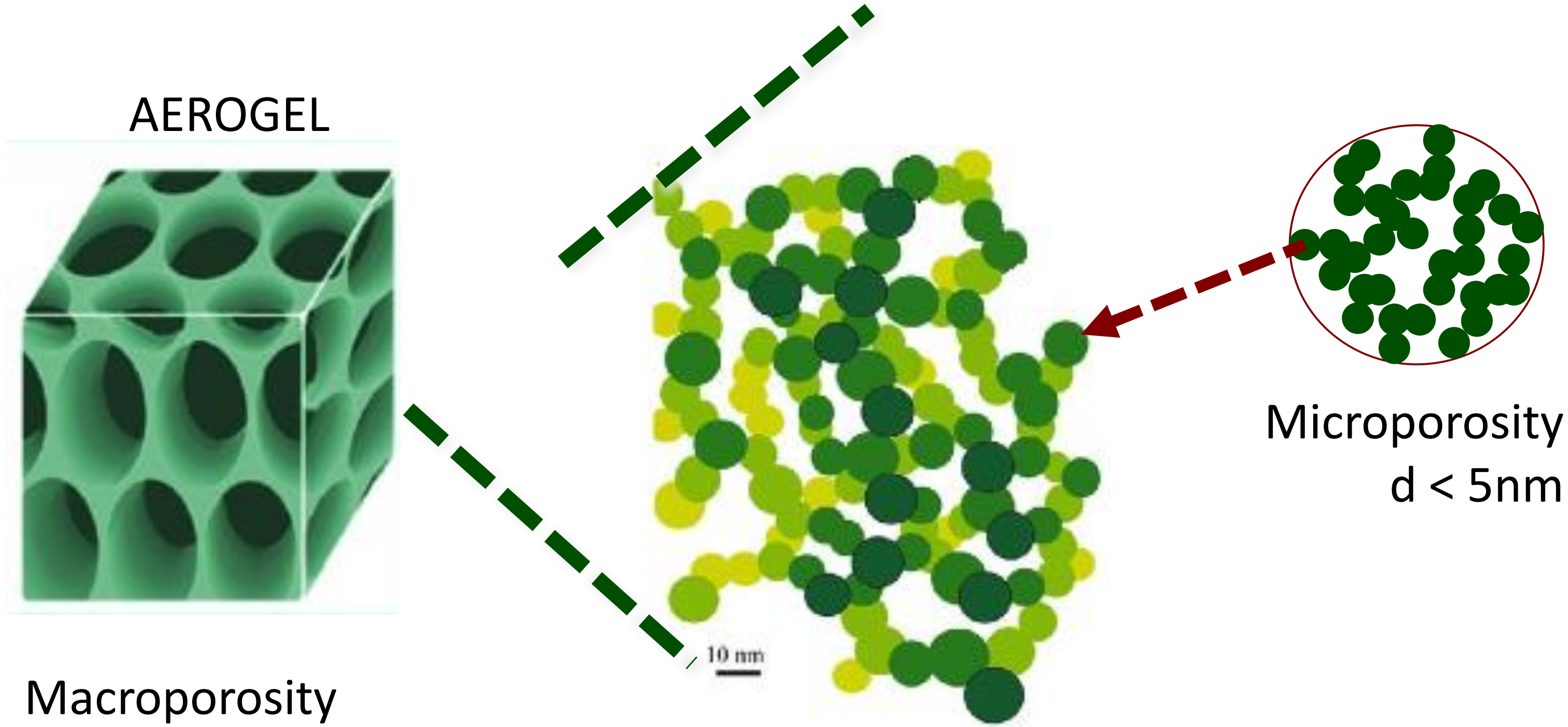
MOF BASED ON AEROGELS

❖ **What is an Aerogel?**

- Extremely porous material, high surface area (> 400 m^2 / g) and low density.
- Obtained by sol-gel technology.
- Maintain their solid and porous 3D structure after the solvent in the pores of the gel is replaced by air.

MOF BASED ON AEROGELS

AEROGEL



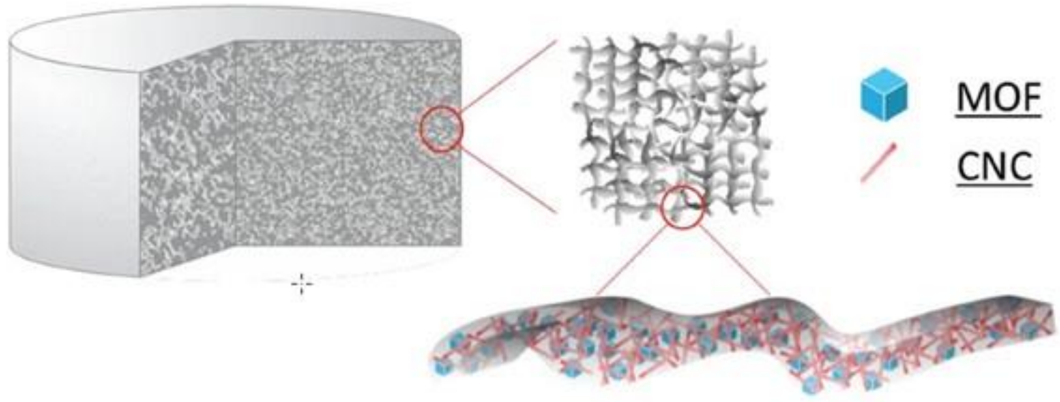
Macroporosity
d > 200nm

Mesoporosity
5 nm < d < 200nm

Microporosity
d < 5nm

MOF BASED ON AEROGELS

- **Why MOF/aerogel?** They have very promising properties in a lot of fields, mainly catalysis and **gas storage**. This is due a better MOF particle distribution, high specific surface, porosity improved for gas flow in the interior parts, numerous adsorption sites.

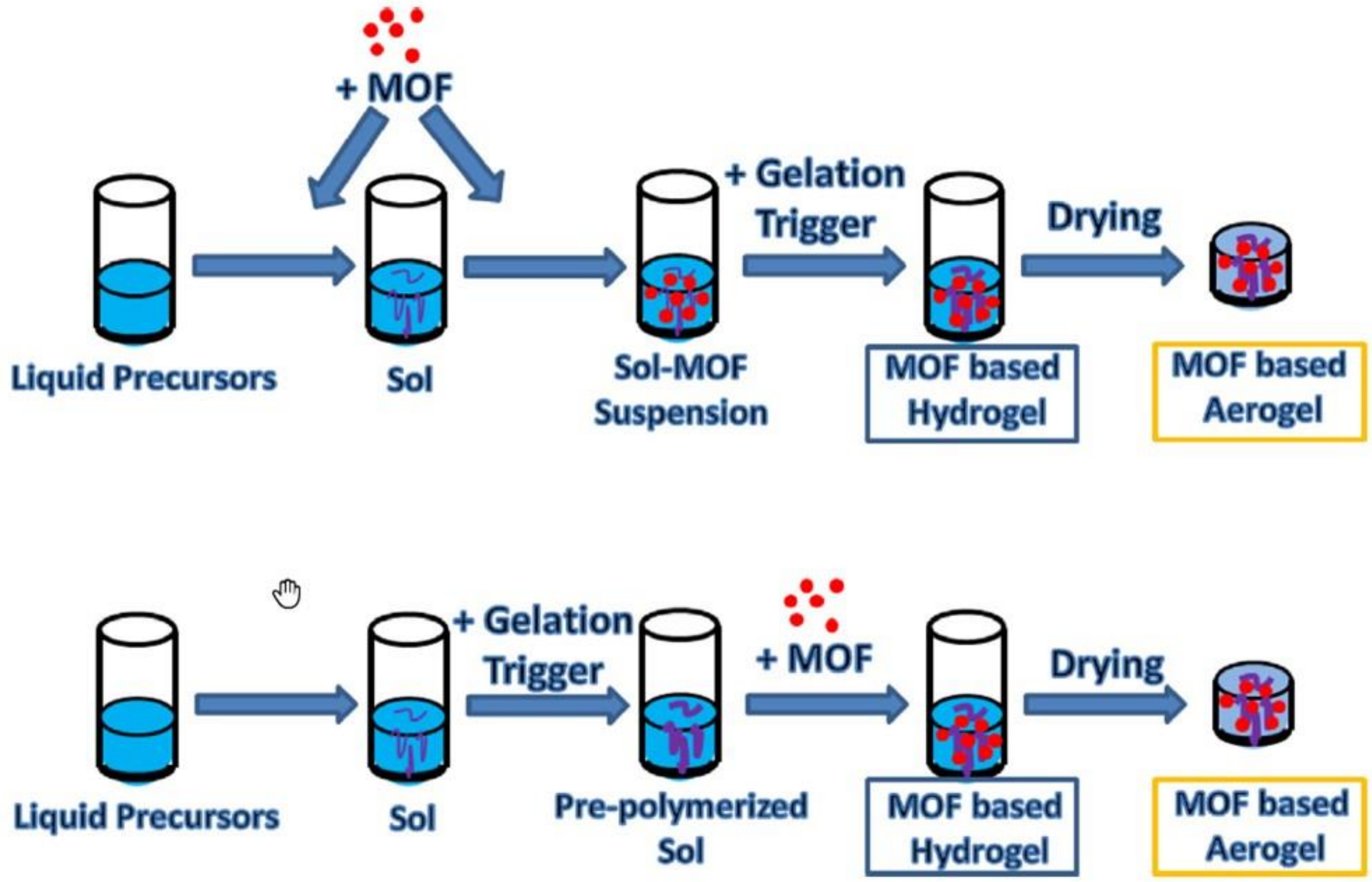


SOURCE; Wang L. et al. Coordination Chemistry Reviews 398 (2019) 213016

The 3D networks can be used to promote the dispersibility of MOFs in hydro/aerogel matrices.

MOF BASED ON AEROGELS

- There is two ways to prepared MOF/aerogel structures: direct mixing of MOF in sol/hydrogel or synthesis “in situ” of MOF in sol phase.

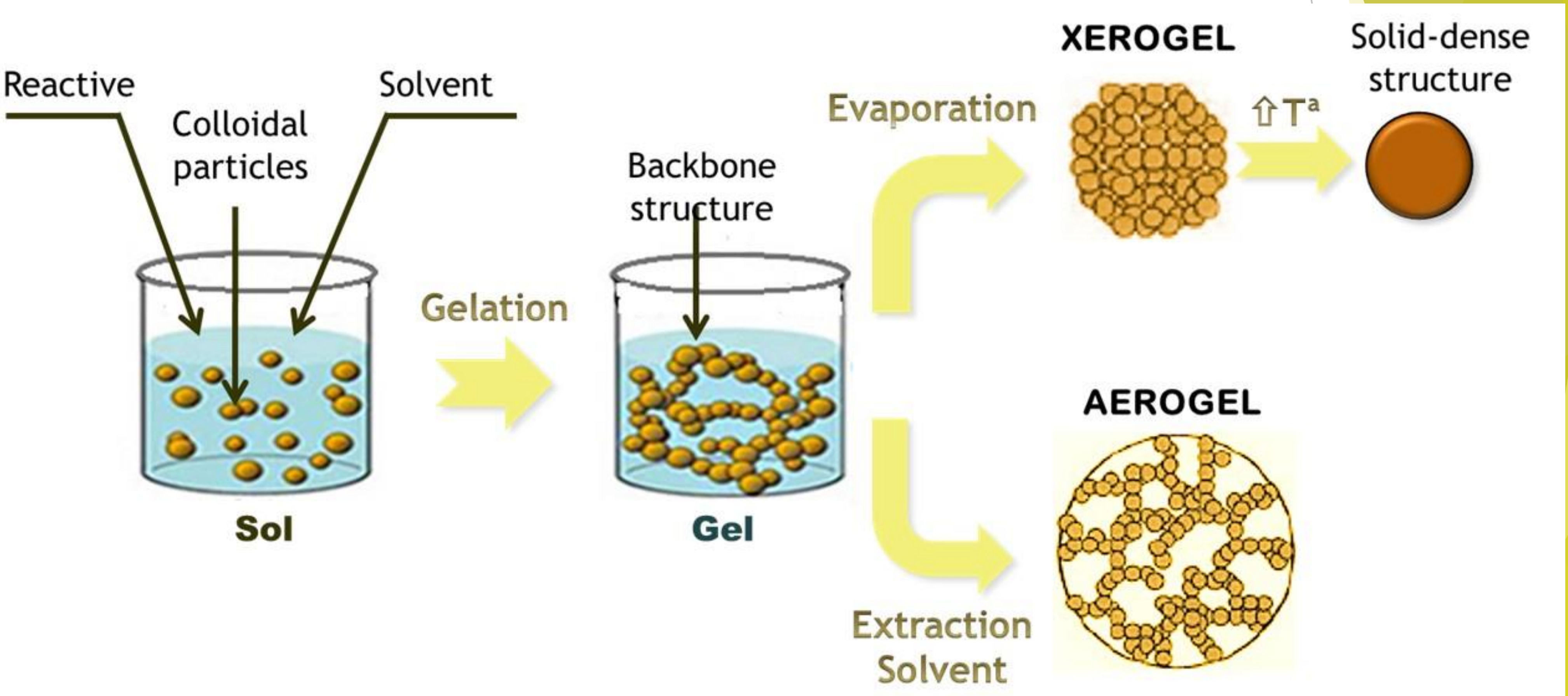


DIRECT MIXING will be applied. Before gelation, hydrogels are modified by adding MOF crystals to the liquid precursor or the sol. The final gelation of the hydrogel matrixes entraps the MOF crystals to produce MOF-based hydrogels.

Besides, by using further supercritical drying or freeze-drying methods, MOF-based aerogels can be obtained.

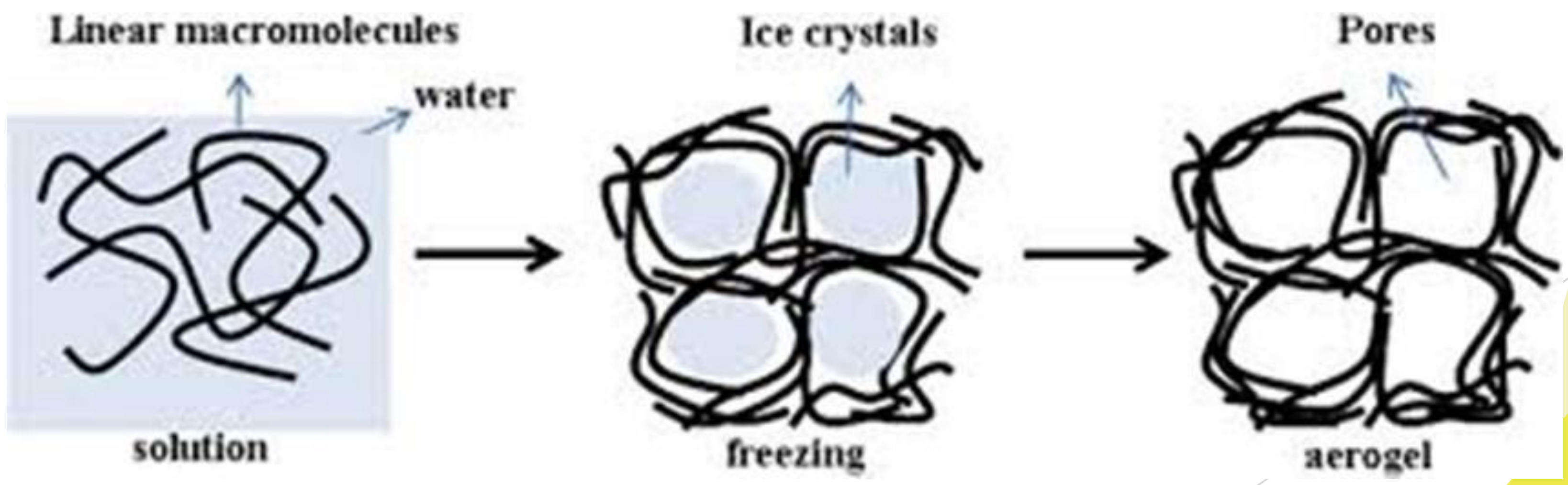
MOF BASED ON AEROGELS

SOL-GEL PROCESS



MOF BASED ON AEROGELS

- Drying of hydrogels is a critical process: sCO2 or freeze-drying. We will choose freeze-drying because is cheaper and it is a widely spread market technology.
- Freezing process is critical in the control of ice crystal size, freezing direction and finally, porous size and morphology.



AEROGELS BASED ON MOF/NANOCELLULOSE

Other Routes for preparing Aerogels based on NANOCELLULOSE :

- ***NFC (Nanofibrillated Cellulose) Aerogels by spray freeze-drying:*** the solution MOF/hydrogel is sprayed in a cryogenic solvent and the droplets are instantly frozen into micro granules. This solution will be prepared by sonication of MOFs in the 1% NFC solution. In the second step, frozen droplets are dried by sublimation (http://dx.doi.org/doi:10.1016/j.carbpol.2016.09.068).

- ***CNC (Crystalline Nanocellulose) Crosslinkable Aerogels***: crosslinkable celluloses were based on aldehyde modified CNCs (CHO-CNCs) and hydrazide modified CMC ($NHNH_2$-CMC) which form hydrazone crosslinks when in contact. The mixture thus contained crosslinked clusters composed of MOFs trapped in CNCs crosslinked to CMC, however these clusters remained colloidally stable. The suspension of clusters will be frozen and freeze-dried to prepare the hybrid aerogels.

- ***CNC (Crystalline Nanocellulose) Aerogels by Ascorbic Acid (AA) reduction:*** the solution of MOF/CNC, previously sonicated, will be mixed with Ascorbic Acid and heated at 80-90°C. After 2 hours gelling will happen. Hydrogel obtained will be freeze-dryed to obtain final hybrid MOF/CNC aerogel.

AEROGELS BASED ON MOF/NANOCELLULOSE

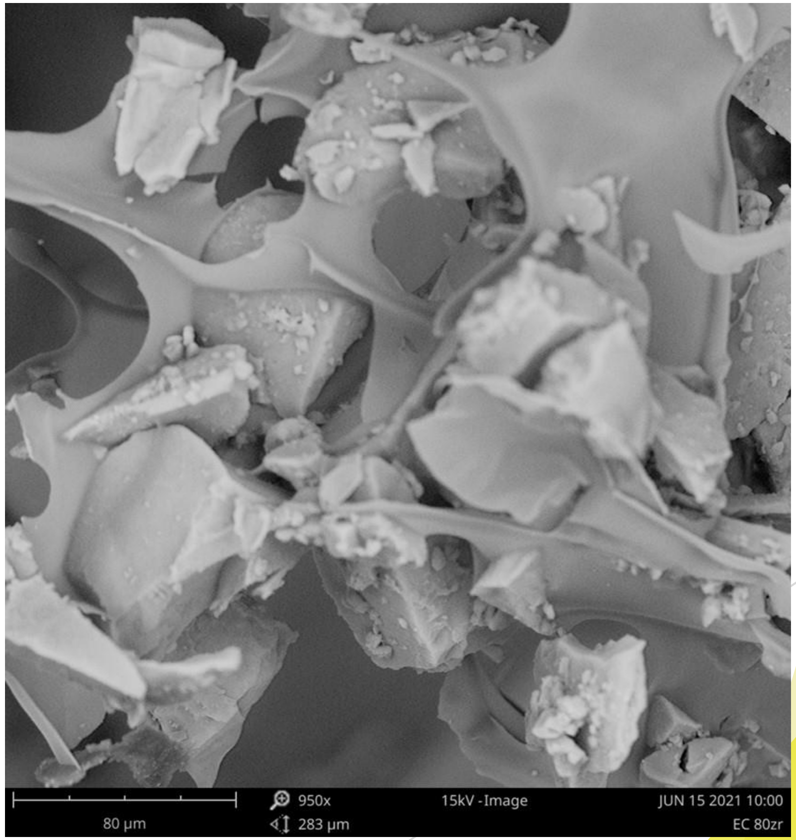
These materials exhibit very low mechanical stability, as the powder was released easily upon delicate handling of the samples. However, some formulation showed very interesting AA adsorption.

AEROGELS BASED ON MOF/NANOCELLULOSE

Other Routes for preparing Aerogels based on NANOCELLULOSE :

Based on the work of Demitri and all*. we prepared cellulose-based foams via microwave curing increasing the MOF load until very high load ratios, as well as mechanical stability.

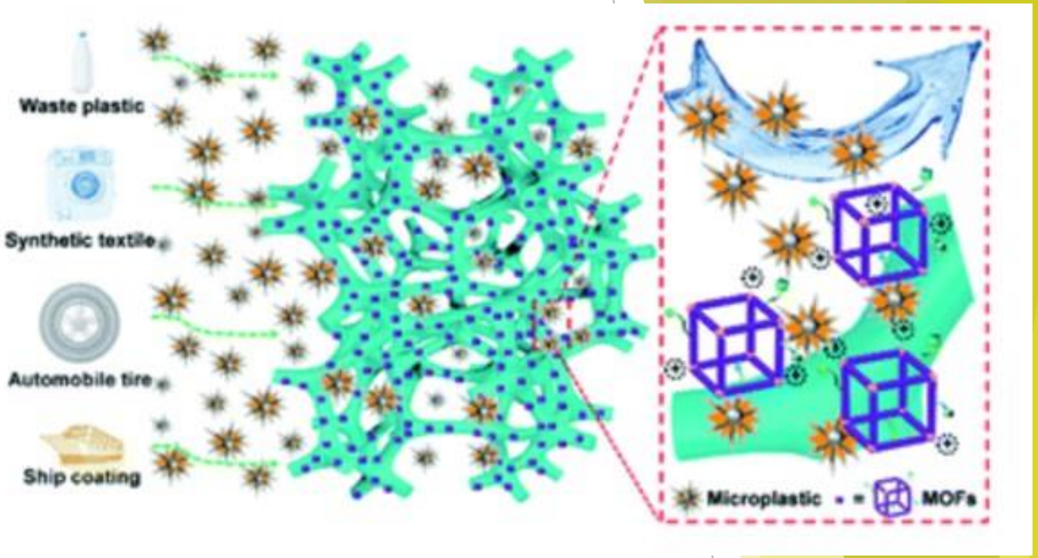
REFERENCE

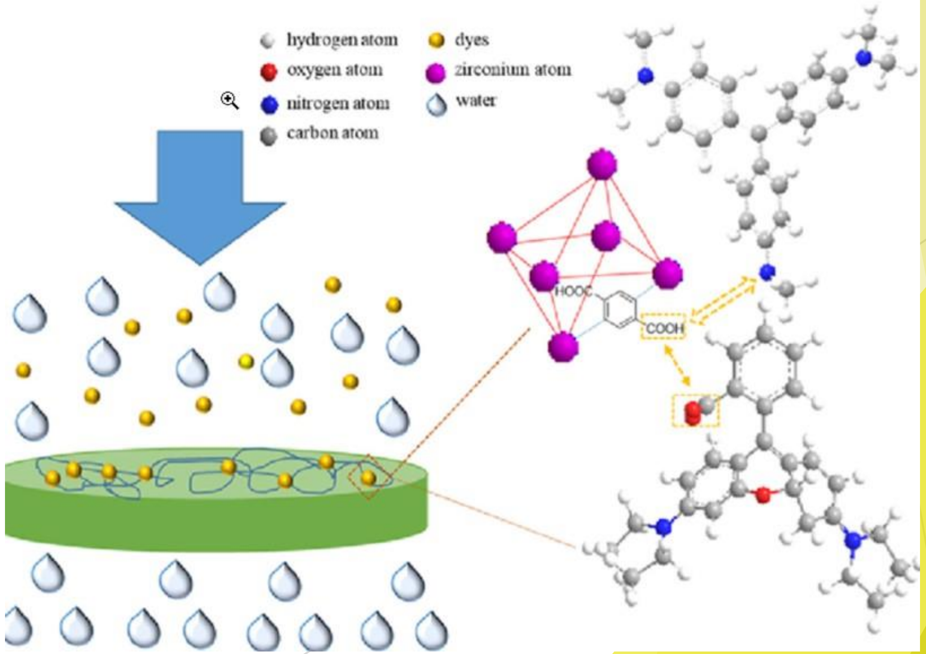


MOF based on foams. Final applications

Foams with MOFs have several applications beyond NEMOSINE:

- Filtration membranes for water treatment, antifouling.
- Catalytic membranes.
- Gas storage (hydrogen, methane, others).
- Efficient removal of microplastics.
- Face masks for gas contaminants.
- Spill treatment in chemical industries.





Thanks for your attention

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