A novel green process for the preparation of high MOF loading paper membrane

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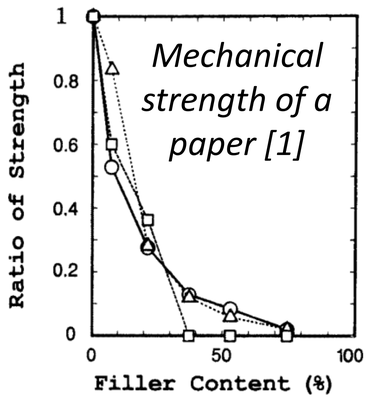
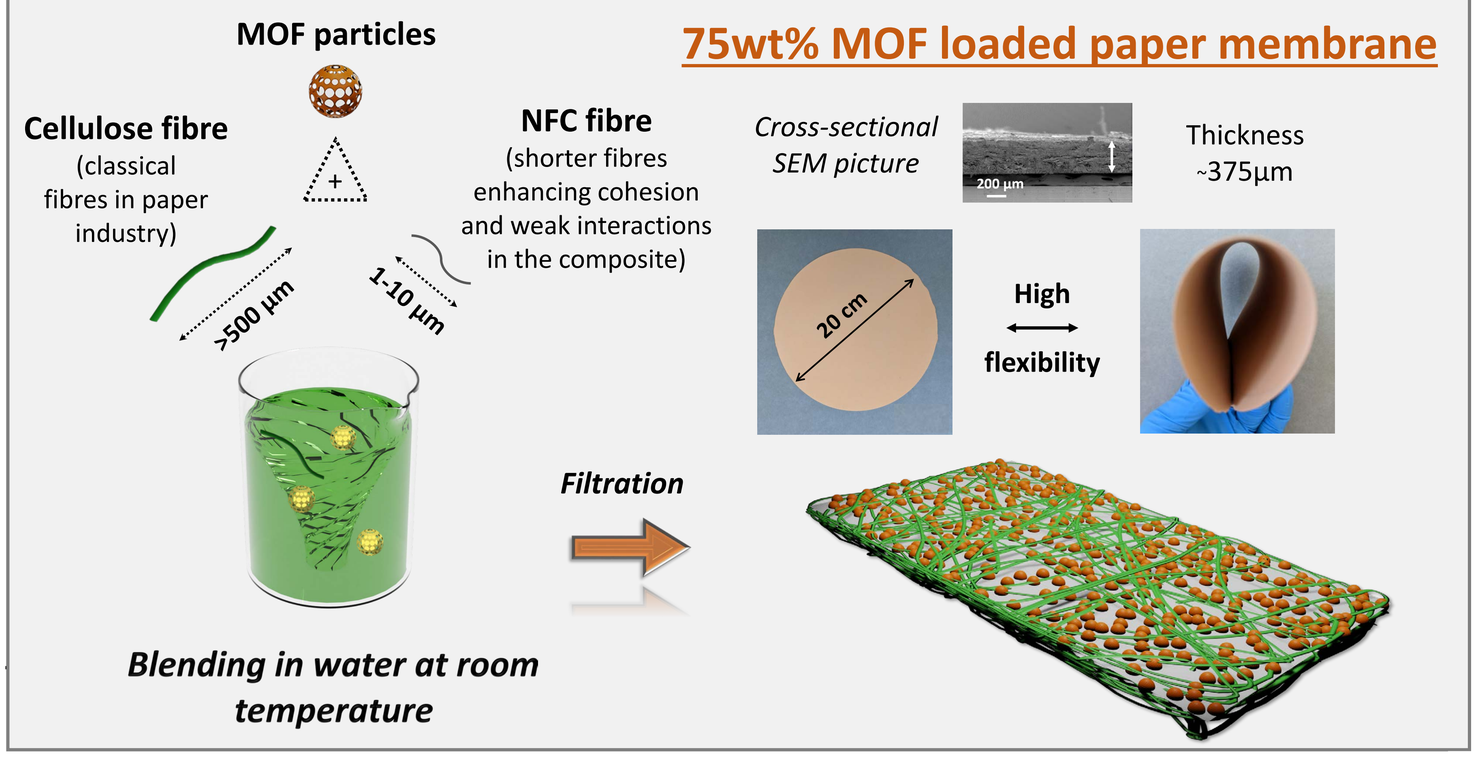
1 Introduction

MOFs are obtained in loose powder form requiring a shaping method for their practical use. Problems are often observed with beads or pellets, monoliths such as structural changes, pore blocking and/or low mass transport properties. To avoid these drawbacks, MOFs can be shaped as a paper.



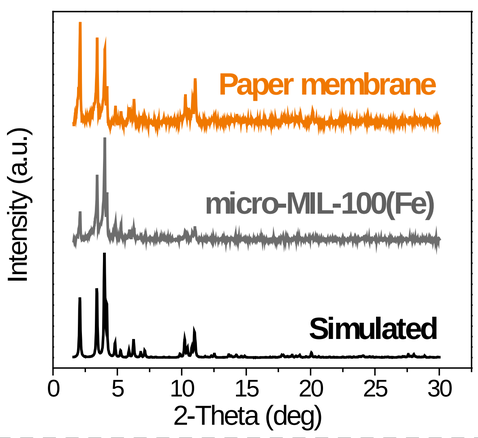
Reaching a high MOF loading (>70wt%) while keeping good mechanical properties remains very challenging. We combined cellulose fibres with Nano-Fibrillated Cellulose (NFC) to improve the inter-fibre bonding. A 75wt% MIL-100(Fe) loaded paper without pore blockage and mechanically stable was obtained.

Scheme of the process

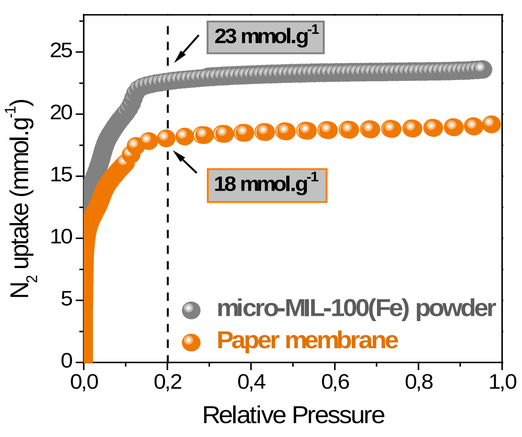


2 Characterizations of the MIL-100(Fe) paper membrane

XRD pattern



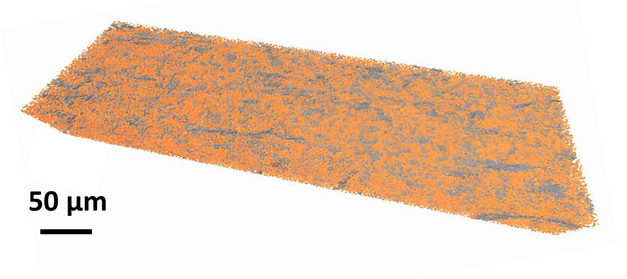
N_2 adsorption isotherm



XRD patterns of the MOF particles before and after shaping remain identical confirming that the process doesn't alter the cristallinity of the particles. The paper membrane degrades starting from 240°C (TGA not shown here). The N_2 adsorption isotherm indicates a fully preserved porosity with a S_{BET} of 1540 vs 1900 $m^2.g^{-1}$ for the MOF powder. Finally, nano-CT scan revealed a homogeneous spatial distribution of the particles and the fibres in the volume.

3D model of the paper membrane based on the CT scanning data

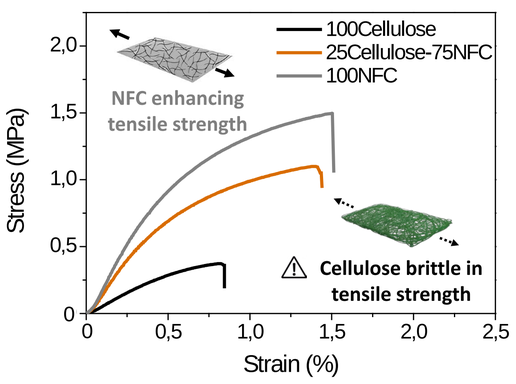
(collab M. Pinto, S. Carvalho, Lisbon)



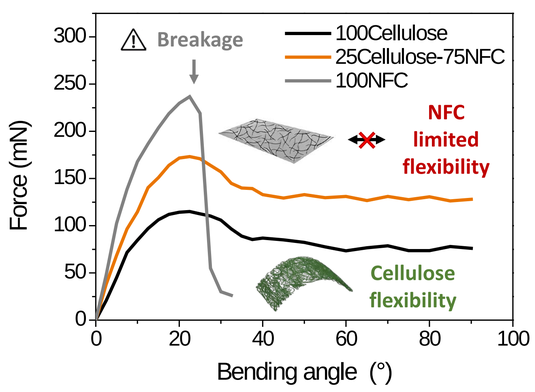
3 Dual-fibre concept

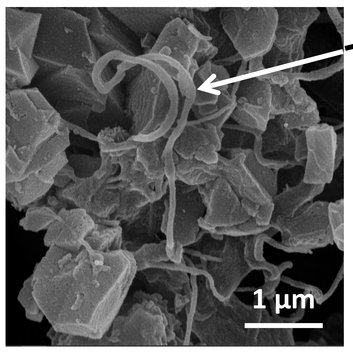
The mechanical properties of the 75 wt% MIL-100(Fe) loaded paper membrane with different ratio of fibres (cellulose:NFC) were investigated by evaluating their tensile strength as well as their flexibility.

Strain-stress curves



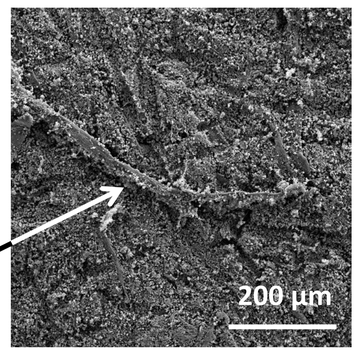
Force vs bending angle curves





NFC fibre interacting at micron level with the particles

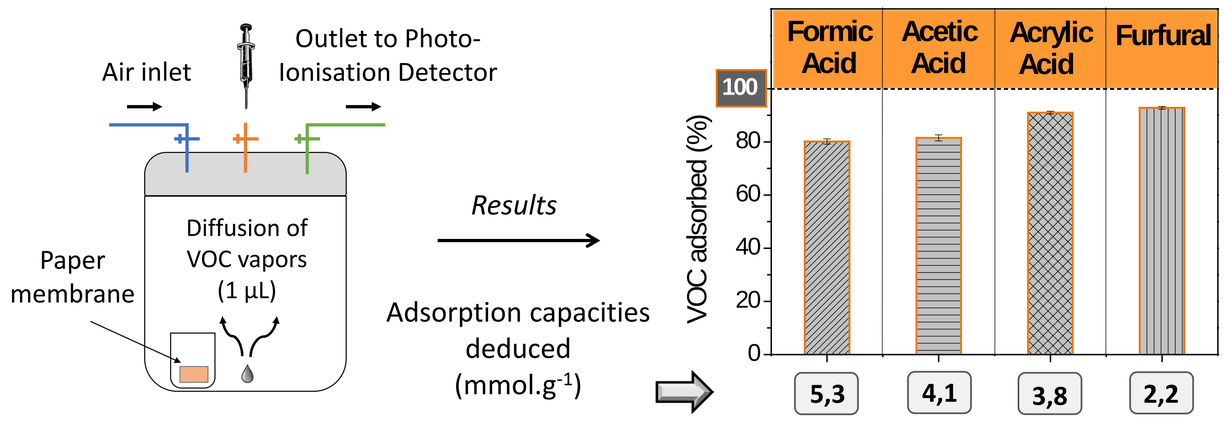
Long cellulose fibre



These results highligth a synergistic effect of the fibres on the mechanical properties of the paper membrane. Conventional cellulosic fibres provide flexibility to the composite, while NFC enhances the mechanical strength by improving inter-fiber bonding and intermolecular bonds with MOF particles.

4 VOCs capture properties

MIL-100(Fe) as powder has been recently identified to selectively trap traces of organic acids through a chemisorption mechanism on Lewis acid sites [2]. We made a set-up to determine the adsorption capacity of the paper membrane with different VOCs (acetic, acid, formic acid, acrylic acid and furfural) in presence of moisture.



5 Conclusion

- ✓ Abundant and inexpensive binder used
- ✓ Rapid, simple, sustainable and scalable process
- ✓ High MOF loading (>70wt%)
- ✓ Capture properties identical to the powder

The paper membrane met all the specifications for a good adsorbent composite and showed high selectivity for the capture of polar VOCs. The next step is to study its seperation performance.

References

[1] : H. Katsuzawa et al. J. Fiber Soc. Japan. 50, 452-457. 1994.
[2] : M. I. Sevrino et al. Angew. Chem. Int. Ed. 62, e202211583. 2023.