

Supplementary Information

Sorbent-Based Atmospheric Water Harvesting: Engineering Challenges from the Process to Molecular Scale

Isaiah Borne* and Andrew I. Cooper

Department of Chemistry, University of Liverpool, Liverpool, L7 3NY, GB

Corresponding Authors: isaiah.borne@liverpool.ac.uk

Table of Contents:

Methods.....	3
MOF-801 and MOF-801 Fiber PXRD.....	5
MOF-801 and MOF-801 Fiber N₂ Isotherm at 77 K.....	6
Energy Burden of AWH in Different Temperature and Relative Humidity.....	7
Example Calculation of Direct Air Cooling vs. Sorbent Based AWH.....	8

Materials: Fumaric acid, zirconium oxychloride octahydrate, formic acid, 1,2-diaminocyclohexane, trifluoroacetic acid, cellulose acetate (CA), and polyvinylpyrrolidone (PVP) were all purchased from Sigma Aldrich. Benzene-1,3,5-tricarboxaldehyde was purchased from Manchester Organics. N-methyl pyrrolidone, petroleum ether, and methanol were purchased from Fischer Scientific. All materials were used as received.

Synthesis and composite fiber fabrication: CC3, MOF-801 and the CC3-CA fibers were synthesized/fabricated according to previous work.^{1,2} The MOF-801/CA fibers were fabricated via syringe extrusion of a polymer dope. MOF-801, cellulose acetate, and PVP were dried in a vacuum oven overnight at 90 °C. A certain amount of MOF-801 was dispersed in NMP and water, vortexed for 30 seconds followed by sonication in a sonication bath for 3 x 30 seconds. The vortex and sonication steps were repeated a total of three times. The polymers (CA and PVP) were then added to the dispersion and left to roll on a vial roller overnight. The homogeneous dope was then extruded into a warm water bath (~40 °C). The fibers were soaked in water for three days, exchanging the water once a day. This was followed by a solvent exchange in methanol for one hour (exchanging methanol every 20 minutes), then petroleum ether (exchanging every 20 minutes). Fibers were allowed to air dry in the fume hood for 2 hours before drying in the vacuum oven overnight at 90 °C. **Table S1** shows the dope composition used to make the MOF-801 fiber.

Table S1: MOF 801/CA Fiber Dope Composition

	NMP	H ₂ O	MOF	CA	PVP
Mass (g)	8.6	1.3	2.5	1.5	0.6

Powder and Fiber Characterization: N₂ and water isotherms were collected for powders and fibers at 77 K and 298 K respectively using a Micromeritics 3 Flex. Around 50 mg of sample was degassed at 100 °C and ~0.01 mbar for 12 hrs. X-ray diffraction patterns were recorded using a Panalytical Empyrean X-ray diffractometer equipped with a Cu x-ray source in transmission mode. Samples were placed on a mylar film and reflection data were collected from 2-60° 2 θ .

Volumetric flow rate calculation: The volumetric flow rate needed to provide 50 L of water for 100 people were calculated by drawing a control volume around the adsorption bed in **Figure 2a** and applying the following assumptions. This process is assumed to be isothermal, the product stream will be air at 100% relative humidity, and the waste stream will be at half the relative humidity of the feed stream. Air in this case was assumed to be nitrogen for ease of calculation. The relative humidity of the feed stream was varied from 10-50% while the temperature varied from 273 K to 313 K. This process was assumed to be steady state so the below equations were used to calculate the volumetric flowrate of the feed stream. F represents the molar flowrate, V is the volumetric flowrate, and x is the mole fraction. The superscripts define the components which are either air or water. Finally, the subscripts show the different streams which are the feed, product, and the waste streams. This system of equations can be extended to include the molar balance of air around the adsorbent bed and then used to calculate the volumetric feed flow rate (V_{feed}).

$$F_{water}^{in} = F_{water}^p + F_{water}^w \quad Eq. S1$$

$$x_{feed}^{water} * V_{feed} = x_{prod}^{water} * V_{prod} + x_{waste}^{water} * V_{waste} \quad Eq. S2$$

$$V_{feed} = V_{prod} + V_{waste} \quad Eq. S3$$

$$x_n^{water} = 1 - x_n^{air} \quad Eq. S4$$

Minimum Energy for Water Extraction Calculation: As described in the manuscript the minimum energy to carry out the water harvesting process delineated in **Figure 2a** was calculated using Equation 1.

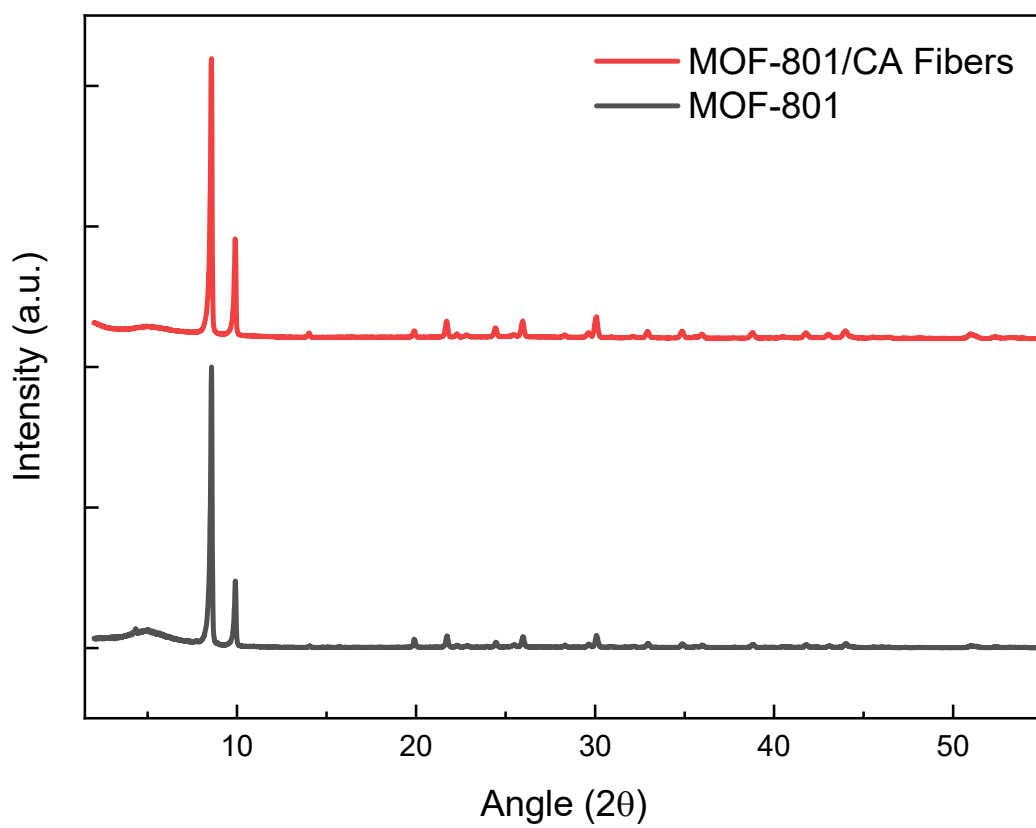


Figure S1: PXRD pattern of MOF-801 and MOF-801/CA composite fibers

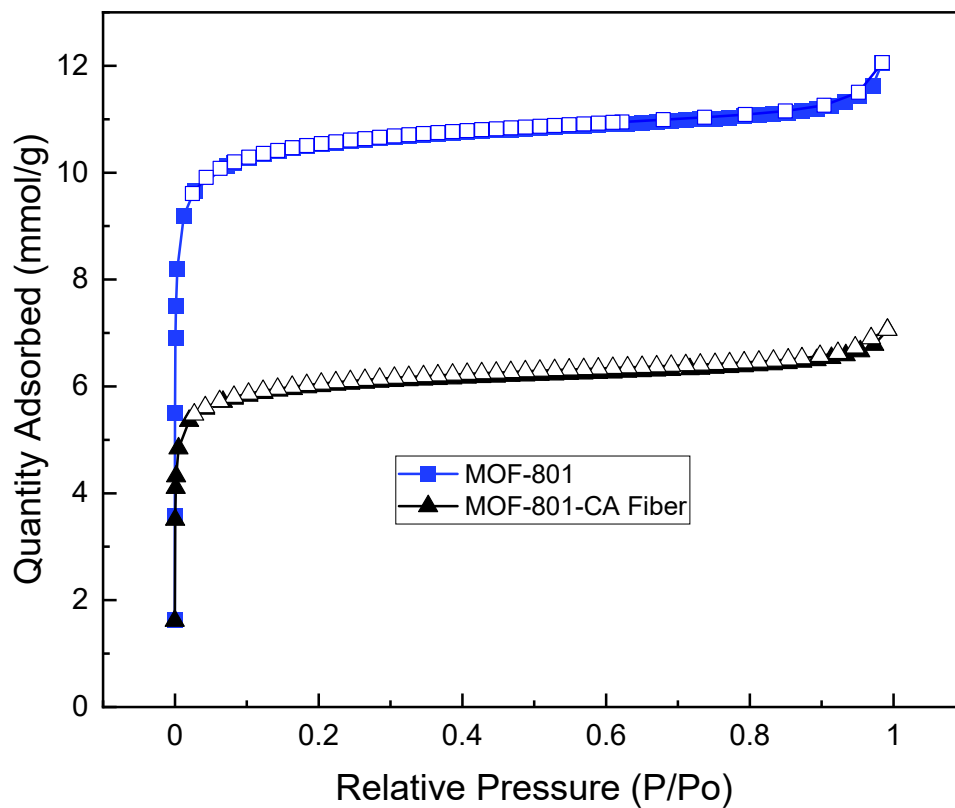


Figure S2: N₂ 77 K isotherm of MOF-801 and MOF-801/CA composite fibers

Table S1: Temperature and Humidity Variation for Global AWH Energy Requirements

	Coldest Hour of Day			Hottest Hour of Day		
	T (°C)	Relative Humidity (%)	Energy (kWh/L)	T (°C)	Relative Humidity (%)	Energy (kWh/L)
Dubai March	18	100	0.89	29	30	2.53
Dubai June	32	60	0.88	41	15	2.67
Dubai September	32	38	1.59	40	23	1.72
Dubai December	21	56	1.92	27	28	3.10
Cairo March	9	66	3.19	15	48	3.42
Cairo June	24	89	0.77	34	36	1.51
Cairo September	24	69	1.17	32	29	2.19
Cairo December	14	67	2.28	20	52	2.25
Jodhpur March	27	47	1.56	38	21	2.23
Jodhpur June	23	83	0.93	37	35	1.29
Jodhpur September	27	94	0.55	34	40	1.32
Jodhpur December	13	64	2.61	24	34	2.99
Nequen March	8	89	2.13	27	26	3.37
Nequen June	2	87	3.18	7	61	4.06
Nequen September	4	65	4.74	15	27	6.87
Nequen December	17	63	2.08	33	18	2.80
El Paso March	8	79	2.58	14	32	5.98
El Paso June	27	39	2.12	38	19	2.49
El Paso September	22	71	1.27	34	20	2.94
El Paso December	1	54	6.97	16	21	8.72

*Historical temperature and relative humidity data reported in **Table 1** and **Figure 1b** collected from wunderground.com. All data is from 2022.

The energy values shown in **Table S1** are based on the calculations shown in the main text in **Figure 2c**.

Energy Burden Calculations

The energy burden of separating cooling air to the dew point of water is as follows. This example examines a scenario of cooling 30 °C air at 20% relative humidity to its dew point of 4.6 °C. Using equation S1 where m is the mass of material to be cooled, C_p is the heat capacity of the material, and ΔT is the difference between the ambient air and the dew point.

$$E = \frac{mC_p\Delta T}{COP}$$

At these conditions and assuming a pressure of 1 bar, water has a partial pressure of around 0.0085 bar. Using ideal gas law we find that there is 0.0061 g of water in 1 L of air and there are about 165,000 L of air needed to provide 1 kg of water. Assuming air has the density of ~1.29 g/L we see that the mass of air to be cooled is around 213 kg. Air has a heat capacity of 1 kJ/kg*K and the change in temperature is around 25.4 °C. Using these values we calculate the energy burden of directly cooling the air to be around 5,400 kJ/kg of water collected. Adding in a typical coefficient of performance (COP) value of 3.5 we see that it takes about 1,540 kJ/kg for direct air cooling.

In the case of sorbent based AWH the minimum work needed to separate water from air with 50% recovery is around 160 kJ/kg. If we include the energy needed to heat MOF-801 to 80 °C to regenerate the sorbent we can arrive at a more realistic energy burden. From previous work⁴³ we know the heat capacity of saturated MOF-801 is ~1.6 kJ/kg*K. If we assume a swing capacity of 0.4 g water per g MOF then we need to heat 2.5 kg of MOF to recover 1 kg of water. With these values added to the initial minimum work needed separate water from air, we calculate an energy burden of ~360 kJ/kg. The energy burden of the sorbent based AWH scenario is 23% of the direct air cooling scenario according to these calculations. Even in realistic conditions accounting for heating efficiency and using a composite as opposed to pure MOF, the energy burden for the sorbent based AWH scenario is much lower than the direct air cooling scenario.

References:

- 1) Hasell, T.; Miklitz, M.; Stephenson, A.; Little, M. A.; Chong, S. Y.; Clowes, R.; Chen, L.; Holden, D.; Tribello, G. A.; Jelfs, K. E.; Cooper, A. I. Porous Organic Cages for Sulfur Hexafluoride Separation. *J. Am. Chem. Soc.* 2016, 138, 1653, DOI: 10.1021/jacs.5b11797
- 2) Aghajani Hashjin, M., Zarshad, S., Motejadded Emrooz, H.B. et al. Enhanced atmospheric water harvesting efficiency through green-synthesized MOF-801: a comparative study with solvothermal synthesis. *Sci Rep* 13, 16983 (2023). <https://doi.org/10.1038/s41598-023-44367-1>
- 3) Jahan, I.; Rupam, T. H.; Palash, M.; Rocky, K. A.; Saha, B. B. Energy Efficient Green Synthesized MOF-801 for Adsorption Cooling Applications. *Journal of Molecular Liquids* 2022, 345, 117760. <https://doi.org/10.1016/j.molliq.2021.117760>.