

## TECHNICAL RESPONSE

## RENEWABLE RESOURCES

# Response to Comment on “Water harvesting from air with metal-organic frameworks powered by natural sunlight”

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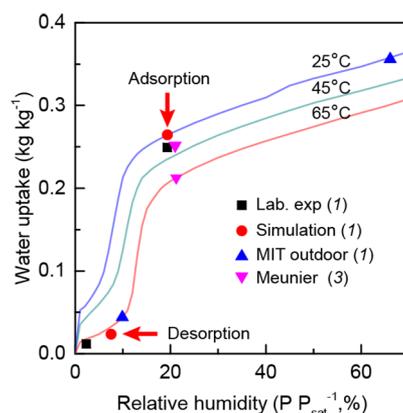
The Comment by Meunier states that the process we described in our report cannot deliver the claimed amount of liquid water in an arid climate. This statement is not valid because the parameters presented in our study were inappropriately combined to draw misguided conclusions.

Our recent study (*1*) discussed metal-organic frameworks (MOFs) as a promising material to harvest fresh water from low-humidity environments with the use of low-grade heat from solar thermal energy. Relative to conventional adsorbents (e.g., zeolites and silica gels), MOFs are promising for water harvesting from air because they can adsorb more water with lower regeneration temperature requirements for its release. Specifically, our study used MOF-801 (*2*) as an example. Here, we address the specific criticisms raised by Meunier (*3*).

The majority of Meunier’s conclusions were drawn from inappropriately combining parameters presented in figures 2 and 4 of (*1*)—namely, the regeneration temperature of 65°C and condenser temperature of 35°C. The conditions presented in our study are summarized in Fig. 1 and Table 1, indicating that none of the conditions from our study [from figures 2, 3, and 4 of (*1*)] coincide with the conditions quoted by Meunier.

First, Meunier states that the condenser temperature in the laboratory experiment (environmental chamber) should have been maintained at 35°C (equivalent to a saturation pressure of 5.6 kPa) with a regeneration temperature of 65°C (incorrectly chosen), and therefore much less water than what we claimed can be harvested with MOF-801. In fact, figure 2 of (*1*) indicates that the

MOF layer was heated to ~83°C, not 65°C, under the experimentally simulated solar irradiance. The objective of the laboratory experiment was to provide controlled conditions to characterize the kinetics of MOF-801 and also validate the theoretical model to predict the optimal performance. The amount of desorbed vapor required to bring the chamber pressure from 1.2 kPa during



**Fig. 1. Adsorption isotherms of MOF-801.**

Water uptake (in kg per kg of MOF) from (*1*) is shown as a function of temperature (25°, 45°, and 65°C) and relative humidity ( $P/P_{\text{sat}}$ , ratio of vapor pressure to saturation pressure). Equilibrium adsorption and desorption conditions for the laboratory isobaric experiment [black square, figure 2 of (*1*)], computational simulation [red circle, figure 3 of (*1*)], MIT outdoor experiment [blue triangle, figure 4 of (*1*)], and conditions quoted by Meunier (inverted pink triangle) are shown. The adsorption and desorption conditions for the computational simulation are labeled. Detailed conditions are described in Table 1.

adsorption [20% relative humidity (RH) at the ambient chamber temperature of ~35°C] to 5.6 kPa during desorption (100% RH at ~35°C) can be substantial, depending on the size of the chamber. As a result, monitoring the rate of desorption is challenging. Thus, isobaric (chamber) experiments allowed us to use a limited quantity of MOF-801 and enabled direct measurement of the condensation/desorption rate. The results validate the theoretical model [which was used to predict the performance in arid regions; see figure 3 of (*1*)]. In practice, our concept relies on vapor condensation at an ambient temperature (100% RH, not 20% RH). Furthermore, as stated in (*1*): “To fully utilize the steep step in water uptake in the MOF-801 isotherm, a temperature difference of ~45°C between the condenser and the layer is necessary to achieve desorption at 10% RH.” This required temperature difference is consistent with Meunier’s comments, which do not add new insight about our study.

However, we note that the regeneration temperature achieved in the laboratory experiment [figure 2 of (*1*)], the ~83°C final desorption temperature with 1 sun, can sufficiently regenerate MOF-801 at the vapor pressure of 5.6 kPa chosen by Meunier (condenser temperature of 35°C leading to desorption at 10% RH). Note that the residual water uptake is even lower than 5 weight percent [figure S6 of (*1*)] at this condition of 83°C and a vapor pressure of 5.6 kPa, given that the adsorption isotherm of MOF-801 shifts down with an increase in temperature. Thus, more than 0.2 liters of water per kg MOF can be harvested at the conditions chosen by Meunier (vapor pressure of 5.6 kPa) and not 0.05 liters per kg MOF as per (*3*). Meunier’s conclusion concerning our laboratory experiment was drawn from an arbitrarily chosen regeneration temperature of 65°C, which is absent from our laboratory experimental data [figure 2 of (*1*)]. A more appropriate regeneration temperature of 83°C should have been used to evaluate the water-harvesting capacity of MOF-801. The cited regeneration temperature of ~65°C in our paper (*1*) referred to the outdoor experiment (MIT roof), where we demonstrated operation with a condenser temperature of ~23°C and an adsorber temperature of ~66°C [figure 4 of (*1*)].

Second, we address Meunier’s concerns on the operating conditions during our proof-of-concept experiments. The MIT roof experiments were not intended to replicate operation in arid conditions; as we clearly state, the RH at the start of the experiment was ~65%. But to demonstrate the viability of our approach with a temperature differential of ~45 K between the adsorber and condenser, we took advantage of the step in the isotherm to sufficiently desorb and condense water. Meunier’s calculations do not account for the fact that the solar irradiance in arid climates is up to ~50% greater than the measured conditions during our experiment, shown in figure 4 of (*1*) (i.e., less than 0.8 kW m<sup>-2</sup>), enabling a temperature difference of >45 K between the adsorber and condenser. In fact, this is supported by our projections of the water-harvesting capacity

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**Table 1. Experimental and computational conditions described in (1).**  $T$ , temperature;  $P$ , vapor pressure; RH, relative humidity;  $\omega$ , equilibrium water uptake based on Fig. 1;  $Q$ , heat flux;  $h$ , heat loss coefficient. Subscripts: ads, adsorption; des, desorption; cond, condenser. RH is calculated from  $P_{\text{ads}}$  and  $T_{\text{ads}}$  or from  $P_{\text{des}}$  and  $T_{\text{des}}$ . Loss includes solar optical/absorption losses.

Conditions	Laboratory exp. [(1), figure 2]	Simulation [(1), figure 3]	MIT outdoor exp. [(1), figure 4]	Conditions quoted by Meunier (3)
<i>Adsorption</i>				
$T_{\text{ads}}$ (°C)	35	25	~25	~35
$P_{\text{ads}}$ (kPa)	1.2	0.63	2	1.2
RH <sub>ads</sub> (%)	20	20	65	20
$\omega_{\text{ads}}$ (kg kg <sup>-1</sup> )	0.25	0.25	0.35	0.25
<i>Desorption</i>				
$T_{\text{des}}$ (°C)	~83	~75	66	~65
$T_{\text{cond}}$ (°C)	~10	25	23	35
$P_{\text{des}}$ (kPa)	1.2	3.17	2.8	5.6
RH <sub>des</sub> (%)	2	8	10	22
$\omega_{\text{des}}$ (kg kg <sup>-1</sup> )	~0.01	0.02	0.05	0.2
$Q_{\text{solar}}$ (kW m <sup>-2</sup> )	1	1	~0.75	Not specified
$Q_{\text{des}} = Q_{\text{solar}} \times \text{Loss}$ (kW m <sup>-2</sup> )	0.91	1	~0.63	Not specified
$h$ (W m <sup>-2</sup> K <sup>-1</sup> )	~9	10	~9	Not specified
Water-harvesting capacity, $\omega_{\text{ads}} - \omega_{\text{des}}$ (kg kg <sup>-1</sup> )	0.24	0.23	0.3	0.05

based on the theoretical simulations with a black-body absorber and humidity conditions relevant to arid climates (20% RH during adsorption). As shown in figure 3 of (1), an adsorber temperature of ~75°C is attainable in an ambient temperature of 25°C with a reasonable effective heat loss coefficient of 10 W m<sup>-2</sup> K<sup>-1</sup> (convective heat loss) and solar flux of 1 kW m<sup>-2</sup>.

Third, we disagree that this design is restricted to a single daily cycle, because continuous operation can be enabled with low-grade heat sources as stated in (1): “Continuously harvesting water in a cyclic manner for a 24-hour period with low-grade heat at 1 kW m<sup>-2</sup>...” Thus, the conclusion that MOF-801 cannot harvest more than 0.05 liters of water per kg MOF is incorrect, as the desorption temperature of ~75°C is sufficient when the condenser is at 25°C [case chosen for the computational model; figure 3 of (1)]. With the optimized MOF layer geometry, continuous operation (e.g., 12 cycles per day) is possible. The references of Meunier’s own work and “modified process design” represent straightforward and logical extensions of our concept. However, they represent only a small subset of the many different and well-understood configurations and scales, such as a portable two-bed-type architecture (4), that can be realized with our concept.

Fourth, we address Meunier’s repetitive claim that a regeneration temperature of 85°C is required for MOF-801. This requirement is valid only if the ambient/condenser temperature is

40°C, enabling a 45 K temperature difference between the adsorber and condenser. As stated in our study, the temperature differential between the adsorber and the condenser dictates the water-harvesting performance, not the regeneration temperature alone. As is evident from the isotherm and the analysis from (1), MOFs with steeper stepwise isotherms can realize more efficient water-harvesting processes with a greater driving potential for regeneration under identical adsorption and desorption conditions [e.g., MOF-841 at ~30% RH (2)]. The performance can be improved in a number of ways, including the evacuated solar collectors suggested by Meunier. Other possible strategies were also discussed in the supplementary material of (1) [e.g., optically transparent and thermally insulating aerogels, pyromark paint, and bubble wrap thermal concentration].

Finally, the water content of dry air is indeed low, 6 g m<sup>-3</sup> (3); simply on the basis of this value, Meunier claims that more than 150 m<sup>3</sup> of air needs to be processed to deliver 1 kg of water. Again, Meunier’s point is unsupported because air processing during adsorption can be well managed through the natural flow of air. For instance, the water content in air for our simulated case (25°C and 20% RH) is approximately 4 g m<sup>-3</sup>. For a conservative estimate, we assume the MOF layer is freely exposed to ambient air flowing onto the layer with a calm wind speed of 0.3 m s<sup>-1</sup>. In this case, the incident vapor mass flux is ~1.2 g m<sup>-2</sup> s<sup>-1</sup> (hourly mass flux of ~4.3 kg m<sup>-2</sup> hour<sup>-1</sup>), which

is already orders of magnitude greater than the vapor mass flux for the adsorption described in figure 3 of (1).

Many other MOFs can be used for water harvesting. CAU-10 (5) and aluminum fumarate (6), both suggested by Meunier, are only two of the many MOFs that have been reported and studied in open literature. Meunier’s recommendations are simply drawn from the adsorption isotherms assuming comparable kinetics with MOF-801. However, adsorption/desorption kinetics can be substantially different for various adsorbents, and detailed studies [extensively discussed in (1)] are necessary. The operational principle, however, does not deviate from what we have described in our study. We believe that our theoretical framework, experimental characterizations, and proof-of-concept prototype (1) can serve as a basis for the development of adsorption-based water-harvesting technologies. We hope that our response clarifies the misinterpretations presented in Meunier’s comments.

#### REFERENCES

1. H. Kim *et al.*, *Science* **356**, 430–434 (2017).
2. H. Furukawa *et al.*, *J. Am. Chem. Soc.* **136**, 4369–4381 (2014).
3. F. Meunier, *Science* **358**, eaao0361 (2017).
4. S. Narayanan *et al.*, *Appl. Energy* **189**, 31–43 (2017).
5. D. Fröhlich, S. K. Henninger, C. Janiak, *Dalton Trans.* **43**, 15300–15304 (2014).
6. J. Canivet, A. Fateeva, Y. Guo, B. Coasne, D. Farrusseng, *Chem. Soc. Rev.* **43**, 5594–5617 (2014).

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