Report summary

This report includes a review and an experimental section. In the review section, we have attempted to examine various materials and considered two types of metalorganic frameworks for the synthesis and initial humidity absorption tests. The metal-organic frameworks were synthesized successfully, and the initial test was carried out at a humidity level of 19% and a temperature of 23°C, followed by a results analysis. The results indicate that the synthesized absorbents are capable of absorbing relative humidity. However, the absorbents are yet to be studied at higher temperatures and humidity levels, which will be the subject of future research.

1) Review

This section attempts to provide an overview of water shortages in various areas. Then, the properties of materials used for humidity absorption are studied. Finally, two materials are selected for and subjected to initial testing.

1.1. Overview

Freshwater shortage is a global challenge that threatens the lives of humans, especially those living in arid areas. Drinking water sources have always been limited in many countries, especially in the Middle East. About half of the world's population is expected to be living under water stress by 2050. Water shortage in desert areas is due to the low precipitation in these zones. A deficit in clean drinking water is a challenge even in areas with adequate precipitation. Although most of the Earth's surface is covered in water, about 96.5% of it is saltwater and cannot be consumed directly. Only about 2.5% of the water on Earth is freshwater, and merely 0.3% of it is liquid. The water in the atmosphere is mainly in the form of clouds, fog, and vapor, the last of which is the dominant form and is found even in deserts. More than 98% of drinking water in Qatar is obtained by desalination, which is costly and energy-consuming. Hence, it is better to develop technologies other than desalination in order to provide sufficient drinking water for such regions. The water in the atmosphere is a potential source of water supply, which has been neglected for long.

There are various methods of extracting water from the air, for instance, atmospheric water harvesting using compression technologies, absorption (or harvesting water from the air), wind turbines for generating electricity and water, and desert plants.

A major issue in harvesting water from air is that there is low humidity in regions inhabited by large populations in dry areas. Relative humidity is usually below 50% in these regions. Another issue is finding a porous material for practically extracting water at low relative humidity and distributing it. The use of absorbents such as silica gel, zeolites, and metal-organic frameworks for harvesting water from the air has constituted a research topic of interest in recent decades.

1.2. Types of absorbents

Atmospheric water harvesting (AWH) is a promising tool in fighting water shortages in dry areas, especially those lacking liquid water resources. The design of materials with such properties as high absorptivity, easy water collection, and long-term recycling capability promises progress in subsequent generations of AWH systems. An absorbent for suitable water harvesting should require low energy for water desorption and be inexpensive in addition to the previously mentioned characteristics. With these properties in mind, we first reviewed some of the materials used for AWH and then selected and synthesized two types of metal-organic frameworks based on the available raw materials and equipment.

1) Silica gel, 2) zeolite, 3) hygroscopic salts, and 4) metal-organic frameworks
Silica gel is one of the most common AWH materials and has polar hydroxyl groups as chemical absorption centers for the formation of bonds between hydrogen atoms and water molecules. As the number of hydroxyl groups on the surface increases, the absorption capability of silica gel can increase due to an increase in the density of the absorption sites. The diameter of the pores in silica gel is usually on the scale of

a few nanometers, and their specific area is about 100-1000 m^2/g, which is suitable for water harvesting.

Another material appropriate for water harvesting from the air is zeolite, which consists of three-dimensional grids of silica and alumina and contains alkaline and alkaline earth metals. In a zeolite, aluminum is the absorption site and is responsible for coordination with water molecules; hence, its amount affects the water harvesting capability. The porosity of the structure of zeolite determines their water harvesting capacity. A larger pore size usually results in a higher water absorption capability.

Nevertheless, the overall water harvesting capacities of silica gel and zeolite are low, at about 0.3–0.5 $\mathrm{kg}_{\mathrm{water}}.\mathrm{kg}_{\mathrm{sorbent}}$–1. Moreover, they require high amounts of energy to desorb water.

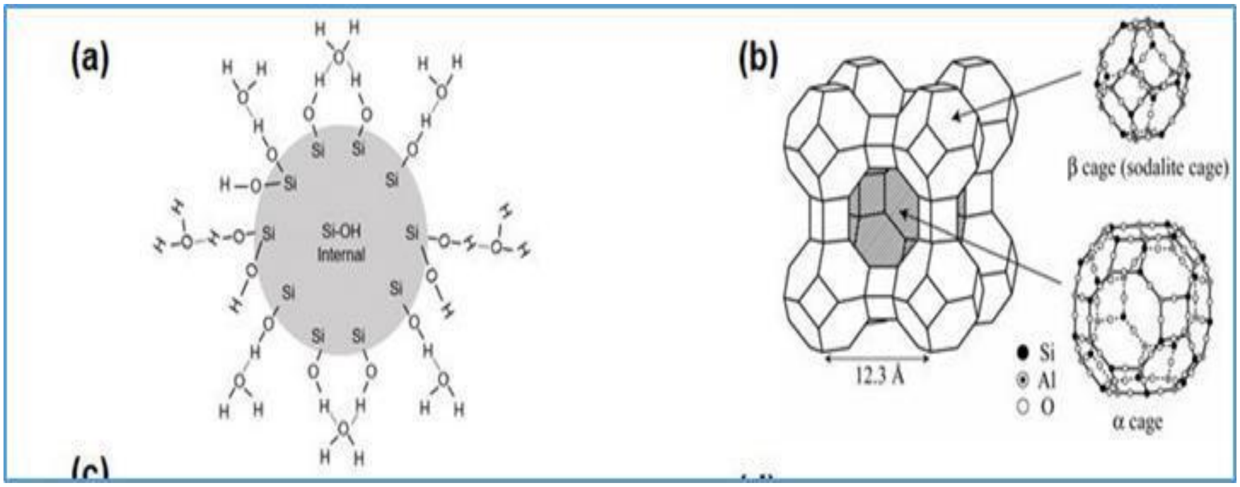

Figure 1. (a) Silica gel; (b) zeolite

Hygroscopic salts can absorb more water at a lower relative humidity; thus, they have better absorptivity than silica gel and zeolite. These substances, such as MgCl2, LiCl, and CaCl2, can harvest water via a hydration reaction but suffer from issues such as particle agglomeration and the formation of an activation layer on the surface of the particles during hydration, which undermines the water vapor permeability and absorption capability. The main problem with these substances is the high energy required to separate water molecules from them, like silica gel and zeolite.

Metal-organic frameworks (MOFs) are porous crystals constructed by inorganic structural centers containing metals and multi-functional organic ligands and coordinate bonds in coherent three-dimensional grids. The highly porous structure of MOFs constitutes numerous potential absorption sites for water molecules. Since the stability, hydrophilicity, and diameter of the pores in MOFs determine their water absorptivity, it is necessary to understand the logical design for MOF-based water harvesting to achieve better performance. The absorption/desorption behavior of MOFs can be adjusted by controlling their hydrophilicity, pore size, and geometry. The hydrophilicity of MOFs may be modified by changing various metals and organic ligands in their structure.

As seen in **Fig. 2**, an increase in the hydrophilicity of MOFs shifts their absorption to lower relative pressure. This indicates that the AWH process may occur at lower relative humidity. The higher hydrophilicity of metal-organic frameworks contributes to AWH since it increases the interactions between the MOF and water molecules.

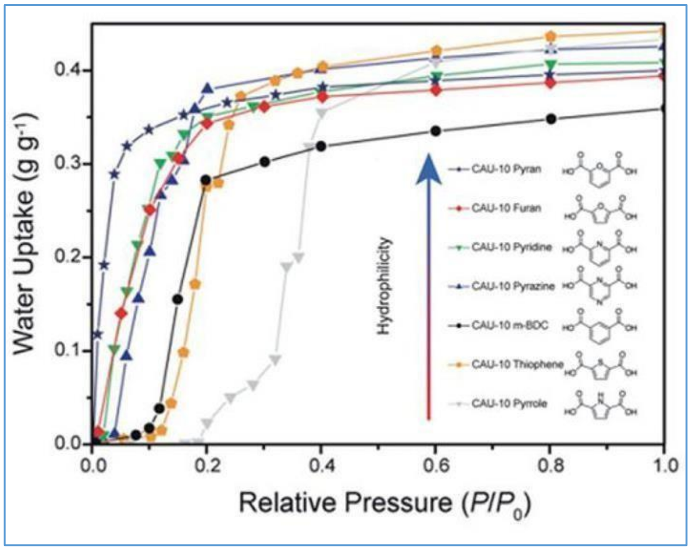

Figure 2. Effect of hydrophilicity on absorptivity

In addition, the pore size of MOFs plays a crucial role in their AWH behavior. An increase in the length of organic ligands can increase the pore size and, hence, maximize the absorptivity. However, this might also increase the energy required to free the absorbed water molecules or affect the porosity of MOFs. These two points must be considered in designing the synthesis, such that absorption and desorption are not adversely affected. **Fig. 3** shows that a longer ligand has improved water harvesting from the air.

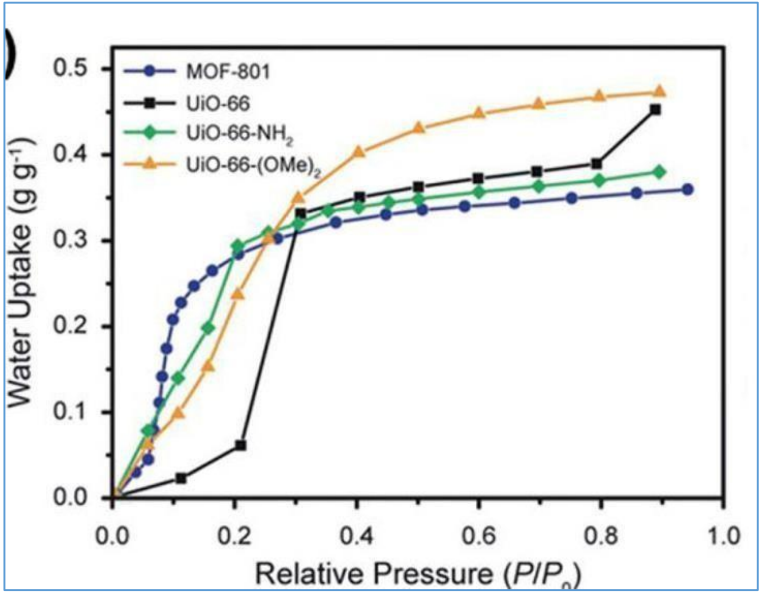

Figure 3. Effect of pore size on absorptivity

Considering the above points, we selected MOF-801 and MOF-808 to investigate the AWH. The main reason for selecting these substances was the availability of their raw materials. They were synthesized for an initial AWH test.

MOF synthesis

2.1. MOF-801

For synthesizing MOF-801, first, 12 mmol of fumaric acid were mixed for one hour with 12 mmol of zirconium (IV) oxide chloride octahydrate in a beaker containing a mixture of DMF solvents and formic acid (20.50 ml) at room temperature. Subsequently, this solution was transferred to an autoclave and placed in an oven at 130°C for 6 h. After 6 hours, the white precipitate was separated via centrifugation and washed 3 times using DMF and ethanol. The resulting solid was then washed 3 times every day for 3 days with 30 ml of DMF so that the solvent is completely removed through the pores. Subsequently, an active sample was prepared by drying the obtained solid in an oven at 150°C for 24 h. **Schematic 1** demonstrates the MOF-801 synthesis steps.

Schematic 1. MOF-801 synthesis steps

2.1. MOF-808

Benzene-1,3,5-tricarboxylic acid (H3BTC (2 mmol)) and ZrOCl2·8H2O (2 mmol) in a solvent mixture of DMF/formic acid (30 mL/30 mL) were placed in a 60-mL screw capped glass jar, which was heated at 135°C for 24 h. Octahedral colorless crystals were collected and washed three times with 10 mL of fresh DMF. As synthesized MOF-808 was rinsed with 20 mL of anhydrous DMF three times per day for 3 days and immersed in 20 mL of anhydrous acetone for 3 days, during which time the acetone was replaced three times per day. Subsequently, an active sample was prepared by drying the obtained solid in an oven at 150°C for 24 h. **Schematic 1** demonstrates the MOF-808 synthesis steps.

Schematic 1. MOF-801 synthesis steps

Note. The MOF-801 sample was synthesized at two different times: one at 24 hours and the other at 48 hours. The synthesis method was identical although the duration of curing at 135°C was different.

Note. Since the autoclave used had a capacity of 100 ml, each synthesis was performed 2 times to obtain an adequate amount of substance.

Note. Since the substances and solvents used are laboratory-grade and have high purity, the cost of synthesizing the substances for testing amounted to about 120USD.

3. Experiment

3.1. Humidity absorptivity of MOF-801

To test the humidity absorptivity of MOF-801, first, we poured 1.4582 g of this substance into a watch glass weighing 23.6562 g and then, placed it inside a box equipped with a thermometer and a hygrometer. **Fig. 4** displays the test steps for MOF-801.

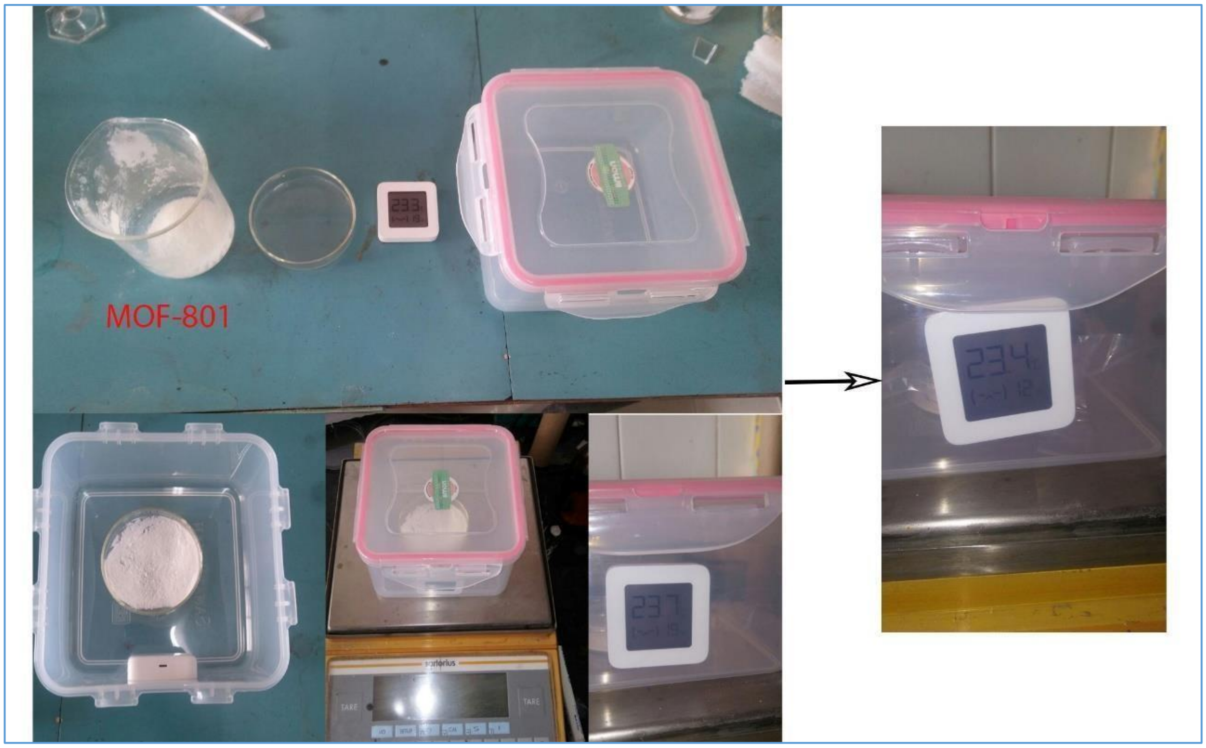

Figure 4. Humidity absorptivity test steps for MOF-801

The temperature and humidity were measured to be 23.3°C and 19%, respectively, before the MOF-801 was placed inside the box. After placing the MOF-801 inside the box, we measured its weight and calculated the absorbed humidity every hour. The corresponding results are displayed in **Fig. 5**. The final temperature and humidity were measured to be 23.4°C and 12%, respectively.

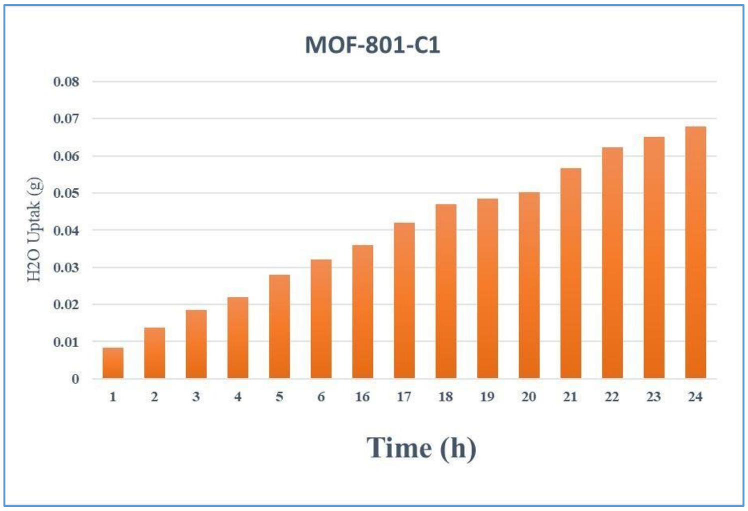

Figure 5. Humidity absorptivity of MOF-801 in the first cycle

As seen in *Fig. 5*, the humidity absorptivity of MOF-801 increased and the humidity inside the box decreased over time. The humidity level after 1 hour reached 12%, indicating the efficiency of the absorbent.

The largest amount of water absorbed by MOF-801 from the air was 0.0680 g, which was obtained after 24 hours. However, the absorptivity was not measured during the night. The absorptivity might have exceeded this amount during the night due to changes in temperature. This must be investigated in prospective research.

To examine the stability and repeatability of the test, we placed the absorbent at 30°C for 2 hours after the first round of testing so that the absorbed water molecules are desorbed and an active absorbent is obtained. Then, the absorption process was repeated under the same conditions (**Fig. 4**). The results are shown on **Fig. 6.**

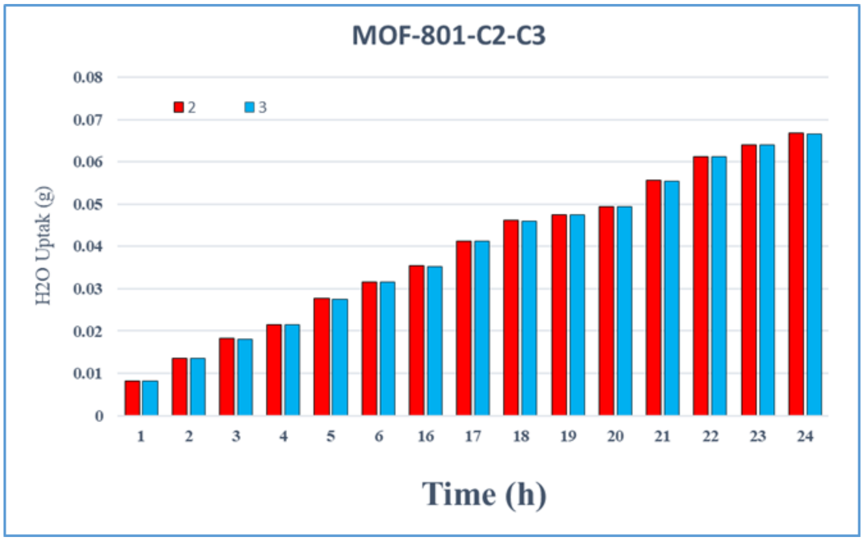

Figure 6. Humidity absorptivity of MOF-801 in the second and third cycles

As seen in **Fig. 6**, the absorptivity has decreased slightly in the second and third cycles. This reduction amounts to 1.75% and 1.96% on average for the second and third cycles, respectively. Given that the test was performed at a humidity level below 20%, the results indicate that MOF-801 is a suitable absorbent for AWH.

Another test conducted on MOF-801 involved leaving the absorbent at 30°C for 2 hours after the third cycle for desorption of the water molecules and then placing 1.4582 g of the absorbent in the box at a humidity of 19% and a temperature of 23°C. However, this time the box was kept open. After 24 hours, the amount of absorbed water was calculated. The results can be seen in the table below.

Absorptivity after 24 hours.	Absorbent
0.0825kg	MOF-801

The humidity absorbed in this case is 0.0145 g more than in the case when the box was closed. This indicates that the absorbent has good humidity absorptivity and will absorb higher amounts of humidity in a location with constant relative humidity. Nevertheless, this needs further investigation under different temperatures and relative humidity levels and more cycles.

3.1.1. Humidity absorptivity of MOF-801 at high humidity and low temperature

A test was performed between 20:30 and 22:30 outdoors to evaluate the efficiency of MOF-801 at high humidity and low temperature. The initial conditions consisted of 26% of humidity and 12.3°C of temperature, as shown in **Fig. 7**. After 2 hours, the humidity reduced to 12%, and the amount of absorbed water was determined to be 0.0936 g. This indicates the good efficiency of the absorbent at low temperature and high humidity. It is worth noting that these conditions are more realistic since the temperature is lower at night.

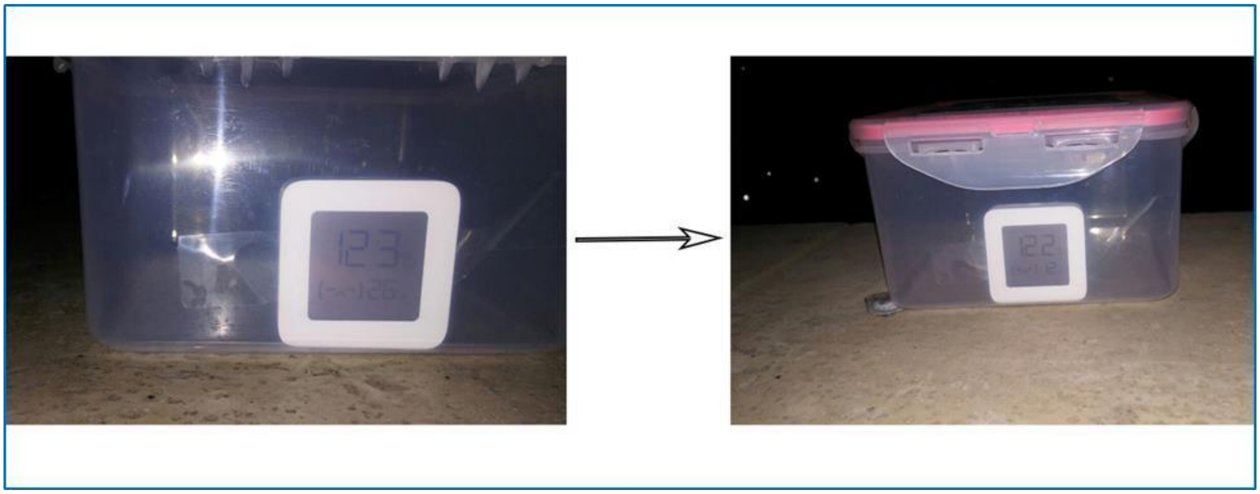

Figure 7. Initial and final absorptivity conditions of MOF-801 at high temperature and low humidity

3.2. Humidity absorptivity of MOF-808

As mentioned previously, MOF-808 was synthesized at 24 hours and 48 hours, and the corresponding samples were respectively designated MOF-808-24 and MOF-808-48. To test the humidity absorptivity of MOF-808-24, first, we poured 1.4582 g of this substance into a watch glass weighing 23.6562 g and, then, placed it inside a box equipped with a thermometer and a hygrometer. The test steps for MOF-808-24 are displayed in **Fig. 8**.

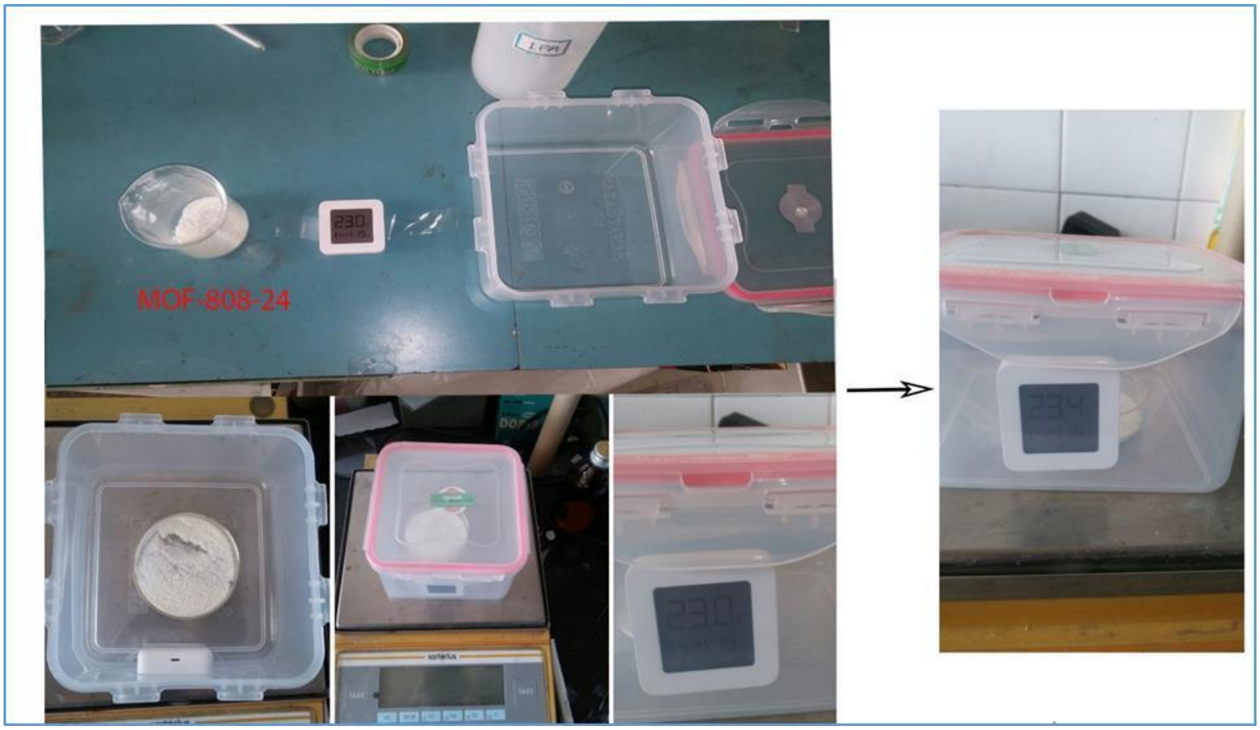

Figure 8. Humidity absorptivity of MOF-808-24 in the first cycle

Fig. 9 shows the results of 2 cycles of water harvesting by MOF-808-24 at a temperature of 23°C and a humidity level of 19%. The results indicate that this absorbent has lower absorptivity than MOF-801 under identical temperature and humidity conditions. The 24-hour absorptivity was obtained to be 0.0401 g, which is 0.0279 g less than that of MOF-801. Moreover, the humidity inside the box reduced from 19% down to 14%.

Since MOF-808 is suitable for humidity absorption at a humidity level above 50%, its lower absorptivity might be due to the fact the test was carried out at a humidity level of 19%. It would be better to study this absorbent also at higher humidity.

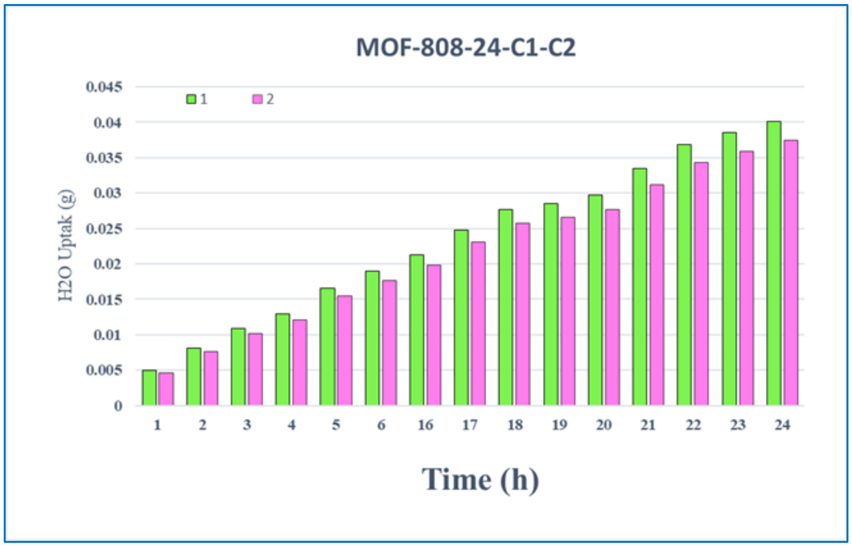

Figure 9. Humidity absorptivity of MOF-808-24

In order to test the humidity absorptivity of MOF-808-48, as before, we first poured 1.4582 g of this substance into a watch glass weighing 23.6562 g and, then, placed it inside a box equipped with a thermometer and a hygrometer. **Fig. 10** shows the results of a cycle of water harvesting by MOF-808-48 at a temperature of 23°C and a humidity level of 19%. The results indicate that the humidity absorptivity of MOF808-48 is slightly (about 2.3%) better than MOF-808-24 under identical temperature and relative humidity conditions.

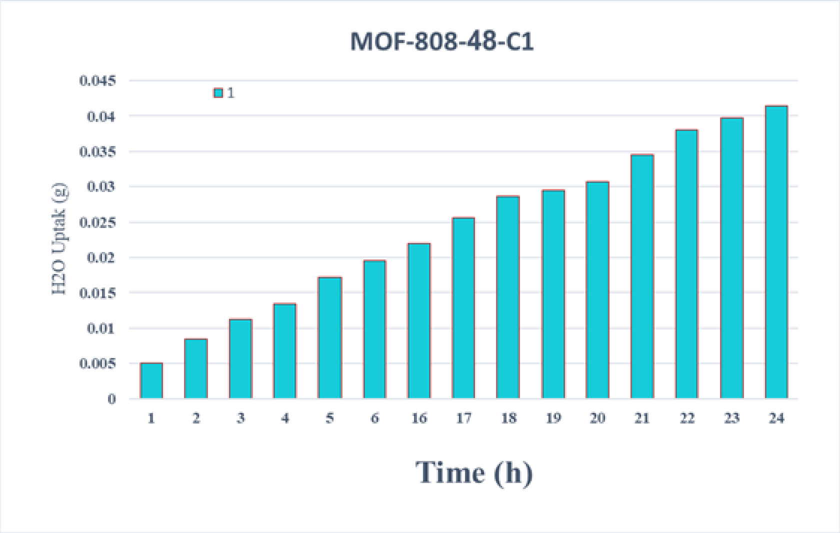

Figure 10. Humidity absorptivity of MOF-808-48

Conclusion

Given the initial results of the two absorbents under different conditions and cycles, one may conclude that it is possible to absorb humidity from the air efficiently using these absorbents. However, this needs further investigation under real (temperature and relative humidity) conditions. Moreover, the amounts of humidity absorbed by these absorbents must be compared to those absorbed by other substances to determine the best absorbent in terms of efficiency and cost. Furthermore, tests should be designed for the desorption of absorbed humidity to establish the ability of materials to absorb humidity from the air and convert it to water. This requires various studies and tests and will be the topic of our future research.

"This report represents the raw, initial documentation of our early experiments before any peer-reviewed publication. It is preserved here for historical and technical transparency."

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