

# Metal-organic frameworks for atmospheric water harvesting: A review of structural and environmental influences

<https://doi.org/10.3126/hp.v13i1.77683>

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**Abstract:** Freshwater scarcity is an escalating global challenge, affecting billions of people despite the Earth's vast water resources. Conventional solutions like desalination and conservation, while useful, are often limited by geographic, economic, or technical constraints. Atmospheric Water Harvesting (AWH) has emerged as a promising alternative to supplement existing water sources, especially in arid and remote regions. Among various materials used for AWH, Metal-Organic Frameworks (MOFs) have attracted significant attention due to their high surface area, tunable porosity, and excellent water adsorption capacity. This review explores the factors that significantly affect water adsorption in MOFs, like pore size, structural defects, hydrophobicity or hydrophilicity, metal center composition, and environmental condition factors such as temperature, pressure and humidity. For instance, larger pore volumes and hydrophilic surfaces tend to enhance water adsorption, and smaller pores result in limited uptake. Similarly, increase in pressure improves the water adsorption in the framework whereas temperature rise cause the water molecules to gain KE which results in lower adsorption and water molecules inside a humid MOF favors further adsorption by increasing its affinity for water molecules. The design and selection of effective materials for atmospheric water harvesting and related applications can be guided by an understanding of how these aspects impact MOF performance.

**Keywords:** Water Scarcity • Atmospheric Water Harvesting (AWH) • Metal-Organic Frameworks (MOFs) • Pore Size • Humidity

Received: 2025-04-17

Revised: 2025-05-17

Published: 2025-05-17

## I. Background

Water is essential for all living organisms on Earth, but only 2.5% of the planet's vast water supply is freshwater. Of that small portion, less than 1% is identified as usable freshwater [1]. Although water covers 71% of Earth's surface, the majority (97.5%) is saltwater, making it unsuitable for direct human consumption or most ecological purposes [2]. But the bigger concern to all mankind is that The World Economic Forum has listed water as a global risk, and according to UN report, as of 2019, more than 3.6 billion of the world population are suffering from lack of sufficient quantity and quality water and

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this number will increase to about 4.8 to 5.7 billion by the end of 2050 [3]. Even in a rich water resource country like Nepal, with more than 6000 rivers and many more water sources, people are facing the problem of water scarcity [4].

One of the primary drivers of water scarcity is rapid population growth and increasing population density, which place tremendous pressure on existing water resources. Researchers and policymakers are actively seeking reliable and sustainable solutions to address the growing water crisis. Controlling the world population, conservation, storage, redistribution, and recycling of available resources are some ways to solve the problem to some extent [5], but the problem has grown so big that mankind are thinking of any alternatives of liquid fresh water on the earth's surface [6]. People started to use seawater after various purification techniques like filtration, distillation and so on. Even though the Earth's surface is predominantly covered by seas and oceans, which account for two-thirds of its expanse, many human communities situated in landlocked areas face an insurmountable challenge when it comes to accessing saline water sources [7]. In this context, the process of extracting water from the atmosphere, known as atmospheric water harvesting (AWH), is emerging as a promising solution [8].

## II. Atmospheric Water Harvesting (AWH)

The atmosphere has water in three phases: the solid phase (ice, snow, and hail), the liquid phase (rain, dew, and fog), and the gaseous phase (water vapor and steam). Solid and liquid forms of water have been used by mankind since time immemorial, but attempts are currently being made to harvest gaseous water for potential future applications [9]. This vast reservoir of atmospheric water could address a considerable portion of water demands for drinking, agriculture, and industrial purposes, positioning the atmosphere as a “rich ore” of water [10]. A variety of approaches are being investigated by different researchers to invent low-cost water harvesting technique for different humidity levels and geographical locations [11].

In general, atmospheric water harvesting technologies may be classified into two large classes: fog water harvesting and dew water harvesting [11]. Fog water harvesting involves intercepting hydrated water droplets or ice crystals that float in the stagnant air above the Earth's surface and are usually formed due to increase in moisture or falling temperature [12]. Whereas the dew water harvesting method attempts to extract all water vapor invisibly evaporating or sublimating from everywhere. Condensation of water vapor on surfaces cooled below the dew point temperature leads to the formation of dew water [13].

Traditionally, atmospheric fog harvesting relies on standard fog collectors (SFCs) and large fog collectors (LFCs). SFCs, typically measuring around  $(1 \times 1)m^2$  with a base elevated 2 meters above the ground, are primarily used for exploratory studies [11, 14]. In contrast, LFCs, generally sized at

$12m \times 4m \times 6m$ , are designed for large-scale water collection, capable of harvesting approximately 150 to 750 liters of water everyday [11, 15]. And, in recent years, researchers have drawn inspiration from animals such as *Stenocara gracilipes* [16], and *Moloch horridus* [17], as well as plants like *Stipagrostis sabulicola* [18], *Opuntia microdasys* [19], and *Lychnis sieboldii* [20] to develop innovative fog water harvesters, which are currently being studied and implemented.

Across the globe, fog water harvesting is simply less attainable than seawater as a viable fresh-water substitute [21], thus making dew water harvesting an ever more important area of research. Dew harvesting techniques find maximum application generally in regions of high humidity or high day-night temperature variation [22, 23]; yet, they also become helpful supplementing freshwater supplies in true arid and semi-arid lands. Rainwater-collecting surfaces painted galvanized steel are commonly used in many parts of the world, with collection rates from 1.9 to 15 liters per day [24]. Black silicon has also been employed to enhance dew harvesting efficiency, as its unique surface morphology promotes effective water collection while reducing evaporation losses [25]. Additionally, porous materials such as zeolites, activated carbon, activated alumina, silica gel, organic materials, and metal-organic composites have been extensively studied as adsorbents [26]. However, in recent years, Metal-Organic Frameworks (MOFs) have emerged as the most promising option among these materials due to their exceptional water adsorption capabilities [27, 28].

### III. Metal Organic Frameworks (MOFs)

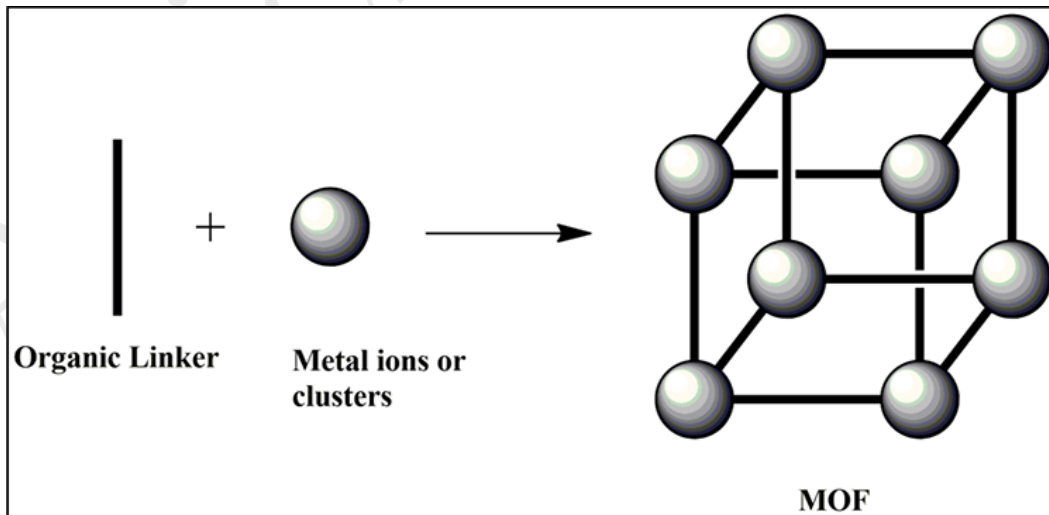


Figure 1. Structure of MOFs [29]

Metal-Organic Frameworks (MOFs) are gaining substantial recognition as a novel category of hybrid porous materials. These structures are crafted by linking metal ions with organic ligands or connectors,

as in Figure 1, and their appeal has grown significantly in recent times [30]. MOFs stand out for their remarkable attributes, which include an exceptionally large surface area, precisely defined porosity [31], customizable composition and structure with adjustability in size [32], versatile functionality [33], high capacity for loading agents [34], inherent biodegradability [35], and improved bio-compatibility [36]. Since the 1990s, the field of MOFs has witnessed remarkable expansion [37] which is evident not only from the extensive volume of research papers published but also from the continuously broadening scope of research within this field. Researchers have demonstrated the versatility of MOFs in a wide range of applications, including clean energy [38], biomedical imaging [39], sensing [40], drug delivery [41], destroying toxic chemicals [42], purifying water [43], magnetic resonance imaging (MRI) [44], gas adsorption [45], among others.

Compared to other porous materials like zeolites, MOFs are considered as the superior options for adsorption for the reasons that zeolites requires high temperature heating for desorption and the pores in zeolite are less than 1 nanometer, whereas the pores in MOFs are larger than 1 nanometer. Also, MOFs' character of large surface area is the most powerful one. The surface area of MOF is between 1,000 to 10,000  $m^2/g$  [46]. To explain this feature of MOF we can say that a single gram of MOF of a size of sugar cube has an internal surface area almost equal to the area of a football field [47]. With several thousand MOFs already structurally characterized and many more yet to be discovered, the field of metal-organic frameworks continues to expand rapidly [46]. Consequently, selecting an appropriate MOF for water harvesting remains a challenging task due to the sheer number of available options.

## IV. MOFs selection for AWH

Optimal moisture harvesting systems should possess a significant moisture adsorption capacity, minimal energy requirements for regeneration, rapid sorption and desorption rates, and enduring cycling stability [8].

First of all, a high sorption capacity plays a crucial role, as it characterises the ability of the moisture absorber to efficiently capture and store atmospheric moisture. This capacity directly determines the volume of captured water that can be achieved [8, 48]. Secondly, low energy consumption during the regeneration process is essential to ensure the sustainability and cost-effectiveness of the entire moisture harvest. Minimizing energy consumption for moisture delivery increases the overall efficiency of the system. In addition, the need for fast sorption and desorption kinetics is of great importance. This feature allows the material to absorb and release water quickly, making it more responsive to variations in atmospheric conditions. Finally, the paramount importance of long-term cycling stability cannot be overstated, as it guarantees the endurance and reliability of the harvester over a long period of time, which ultimately reduces maintenance and replacement costs [8].

This review aims to provide an overview of the main factors that affect water adsorption in metal-organic frameworks (MOFs), including pore size, defects, hydrophobicity, metal type, and environmental conditions like pressure, temperature, and humidity. Based on recent studies, it summarizes how these factors influence water uptake and stability, helping to guide future research and practical use of MOFs in water-related applications.

## V. Factors Influencing Water Adsorption in MOFs

Water adsorption in metal-organic frameworks (MOFs) is governed by a variety of structural and environmental factors. Understanding how these factors influence water uptake is essential for improving the performance of MOFs in applications such as water harvesting, humidity control, and energy storage. This section discusses the key elements that affect water adsorption behavior of any MOF.

### Structural Factors

The water adsorption capacity of MOFs is fundamentally governed by their structural properties, which include pore architecture, framework defects, hydrophobicity, and the nature of metal nodes. These intrinsic features collectively determine the host-guest interactions and adsorption efficiency.

#### Effect of pore size, defects, and hydrophobicity

**Table 1.** Comparison of total water uptake ( $\eta_{water,total}$ ) measured during the first adsorption branches on the basis of pore sizes ( $d_{pore,NLDFT}$ ) of  $Ni_2L$  materials determined from nitrogen sorption data at 77 K [49]

Frameworks	$d_{pore,NLDFT}$ (Å)	$\eta_{water,total}$ (mmol.g <sup>-1</sup> )
Ni <sub>2</sub> dhtp	12.73±0.22	29.89±0.96
Ni <sub>2</sub> dhip	11.93±0.30	22.69±3.27
Ni <sub>2</sub> bpp	16.68±0.57	31.67±1.20
Ni <sub>2</sub> bpm	18.52±0.52	41.82±4.00
Ni <sub>2</sub> tpp	25.09±0.67	47.91±4.04

Kloß et al. (2024) [49] investigated the  $Ni_2L$  framework series (where  $L$  represents different linkers: dhtp, dhip, bpp, bpm, and tpp) to examine the effects of pore size and linker hydrophobicity on water adsorption. Their findings revealed that defects in  $Ni_2dhtp$  diminish adsorption capacity by limiting hydrogen bonding sites, whereas a lower defect concentration leads to more consistent adsorption behavior. However, defect effects become negligible in larger pores. At low pressure, water initially binds to open metal sites, forming clusters that connect through hydrogen bonding, leading to pore condensation, which is influenced by pore size and hydrophobicity. Smaller pores form asymmetric hydrogen bonds with water, which tends to make it interact more with the framework, while larger pores tended to favor the arrangement of the water as resembling that of a bulk fluid, dominated by water-water interactions. As the pore size grows larger, the dehydration temperature drops, suggesting reduced confinement effects.

In general, pore size, structural defects, and hydrophobicity are key factors influencing water adsorption and molecular arrangement in these MOFs. Table 1 shows the comparison of total water uptake based on various linker and pore size, demonstrating how these factors influence the water uptake behavior in  $Ni_2L$  materials.

### Effect of metal nodes

Keshavarz (2023) [50] reported that metal centers altered the water-stability property of MOFs by determining the strength of interactions with the water molecules, hydrolytic stability, and structural integrity during adsorption. Stronger types of these interactions, such as coordination bonds, hydrogen bonding, and van der Waals forces, can improve water uptake but can also create stronger bonds, making desorption difficult and having an adverse impact on regeneration efficiency. In addition to that, hydrolytic stability is also essential because some metal nodes, especially the ones formed by Fe, will hydrolyze in the presence of water and cause the MOF to degrade. The reduction in long-term adsorption performance because water uptake distorts the metal nodes and displaces ligands, altering the structure and adsorption mechanism. Such an outcome evidenced that metal node selection should be balanced between strong water interactions and sufficient stability and reversibility so that the MOF has a high adsorption capacity, structural robustness, and regeneration over many cycles.

The work carried out by Furukawa et al. (2014) [48] demonstrated that zirconium-based MOFs, notably MOF-801 and MOF-841, display remarkable hydrolytic stability due to the superior secondary building units (SBUs) of  $Zr_6O_4(OH)_4$  which is able to resist structural degradation under several adsorption-desorption cycles. Unlike copper- or iron-based MOFs—which retain their porosity and structural integrity in water because of their strong metal-ligand interactions—Zr-based MOFs tend to degrade, losing their framework stability upon hydrolysis. Strong coordination between Zr and O atoms in the SBU inhibits breakage of the whole metal-ligand framework, thus granting Zr-based MOFs hydrolytic stability. Furthermore,  $\mu_3$ -OH groups in these MOFs stabilize the MOFs by forming hydrogen bonds with water molecules, thereby enhancing the adsorption.

Han et al. (2024) [51] studied mixed-metal MOF-74-MgNi and demonstrated how mixed-metal nodes influence water adsorption performance by enhancing both capacity and stability. Their findings showed that MOF-74-MgNi-2, synthesized by optimizing the metal composition and synthesis conditions, exhibited superior water adsorption properties compared to its single-metal counterparts, MOF-74-Mg and MOF-74-Ni. Notably, at lower moisture pressure ( $P/P_0 = 0.1$ ), MOF-74-MgNi-2 achieved a water adsorption capacity of 0.44 g/g, which was 0.12 g/g and 0.10 g/g more than that of MOF-74-Mg and MOF-74-Ni, respectively. The improved adsorption was attributed to defect sites in the metal cluster, which created a localization of electrostatic potential at unsaturated cation sites, ultimately strengthening interactions with polar water molecules. Furthermore, the thermal breakdown temperature was above 250°C, ensuring stability under thermal cycling, with water adsorption-desorption tests confirming that

its capacity decreased by only 9.0% after 10 cycles. Hence, these findings strongly suggest that metal node composition and defect engineering are key in tuning MOFs for water adsorption applications and affect both uptake efficiency and prolonged mechanical stability, which are two crucial factors for atmospheric water harvesting and thermal energy storage.

### Other Structural Modulators

Apart from pore size, structural defects, hydrophobicity, metal nodes, and environmental conditions like temperature, pressure, and humidity, several other factors can significantly influence water adsorption in MOFs. The presence and nature of functional groups on the organic linkers is one such parameter; polar functionalities can strengthen the water affinity via hydrogen bonding [52]. The topological arrangement and dimensionality of pore networks—in particular, 1D channels versus 3D interconnected pores—further influence water accessibility and diffusion [53]. Furthermore, flexibility of certain MOFs leads to dynamic variations in pore volume during adsorption, which greatly affects their uptake capacity and kinetics [54]. Crystal size and morphology can also have an effect; smaller crystals or nanostructures tend to facilitate fast sorption due to short diffusion pathways. The adsorption-desorption cycling stability of a MOF is an important factor often disregarded [55, 56]. Framework fatigue, pore collapse, hydrolysis, or irreversible water retention can occur during subsequent cycles, which in turn would impede performance through time. Finally, mixed-linker and mixed-metal MOFs can significantly enhance its water uptake capacity, adsorption-desorption kinetics, and cycling stability, enabling effective atmospheric water harvesting under low humidity conditions [57].

### Environmental Factors Affecting MOF Performance

Beyond intrinsic structural properties, external environmental conditions—such as pressure, temperature, and humidity—play a critical role in modulating the water adsorption behavior, stability, and practical applicability of MOFs.

#### Effect of pressure

The water uptake capacity of porous materials, such as metal-organic frameworks (MOFs), is highly dependent on the applied pressure. As the pressure or relative pressure ( $P/P_o$ ) increases, the adsorption of water molecules within the pores rises significantly, might start to saturate after a certain value in some cases [58]. This trend is primarily driven by enhanced condensation and pore filling at higher pressures [48]. The effect is especially notable in MOFs featuring hydrophilic functional groups or open metal sites, where strong interactions with water molecules significantly boost adsorption at elevated pressures [59, 60].

Furukawa et al. (2014) [48], studied water adsorption in various MOFs, revealing a strong dependence of their water uptake capacity on pressure. Table 2 shows the increasing water uptake with rising



$P/P_o$  across different zirconium-based frameworks. For instance, MOF-808 shows a steep uptake increase from  $55 \text{ cm}^3/\text{g}$  at  $P/P_o = 0.1$  to  $735 \text{ cm}^3/\text{g}$  at  $P/P_o = 0.9$ . This table also shows the difference in uptake capacity of various MOFs within the same pressure range, for example, at a relative pressure of  $P/P_o = 0.9$ , MOF-802 exhibits a water uptake of only  $110 \text{ cm}^3/\text{g}$ , whereas, Mg-MOF-74 demonstrates a significantly higher capacity—exceeding it by more than 6.5 times under same conditions. This can be credited to several structural and chemical factors. One important reason is the pore size of the MOF, which, if large enough, allows the inclusion of water molecules due to water’s small kinetic diameter ( $2.6 \text{ \AA}$ ). However, limited water uptake at lower relative pressures suggests a low affinity of water to some MOF surfaces. This is mainly due to the hydrophobic nature of certain organic linkers, which require higher water vapor pressures to initiate pore filling. On the other hand, MOFs with more hydrophilic surfaces or larger pore volumes show higher water uptake at elevated pressures, highlighting the strong relationship between porosity and total water adsorption capacity.

**Table 2.** Summary of the adsorption capacity of various zirconium-based MOFs [48]

MOFs	Water Uptake, $\text{cm}^3/\text{g}$		
	$P/P_o = 0.1$	$P/P_o = 0.3$	$P/P_o = 0.9$
MOF-801-P	280	380	450
MOF-802	35	70	110
UiO-66	20	125	535
MOF-808	55	160	735
MOF-841	10	550	640
MOF-804	160	235	290
MOF-805	25	160	415
MOF-806	30	60	425
Mg-MOF-74	550	605	750
Co-MOF-74	505	565	630
Ni-MOF-74	490	545	615

### Effect of temperature

The adsorption capacity of MOF for water is highly dependent on temperature. Solovyeva et al. (2018) [61], studied the temperature-dependent water uptake behavior of MOF-801 and found that higher adsorption temperatures lead to lower equilibrium uptake values. As can be seen in Table 3, for each grain size and surface-to-mass ( $S/m$ ) ratio studied, uptake is found to be highest at  $20^\circ\text{C}$  and becomes gradually lower with increasing temperature up to  $35^\circ\text{C}$ . For instance, at  $S/m = 4.4 \text{ m}^2/\text{kg}$  and grain size  $0.8 \text{ mm}$  to  $0.9 \text{ mm}$ , the uptake decreased from  $0.28 \text{ g/g}$  at  $20^\circ\text{C}$  to  $0.18 \text{ g/g}$  at  $35^\circ\text{C}$ . The highest uptake for this MOF is at the lowest temperature ( $20^\circ\text{C}$ ) and highest grain size ( $0.8 - 0.9 \text{ mm}$ ). This trend reflects the exothermic nature of the adsorption process, where higher temperatures reduce the material’s affinity for water vapor. Similarly, an increase in temperature boosts the kinetic energy of  $\text{H}_2\text{O}$  molecules, allowing them to overcome their interaction forces with the framework resulting in reduced uptake [62].

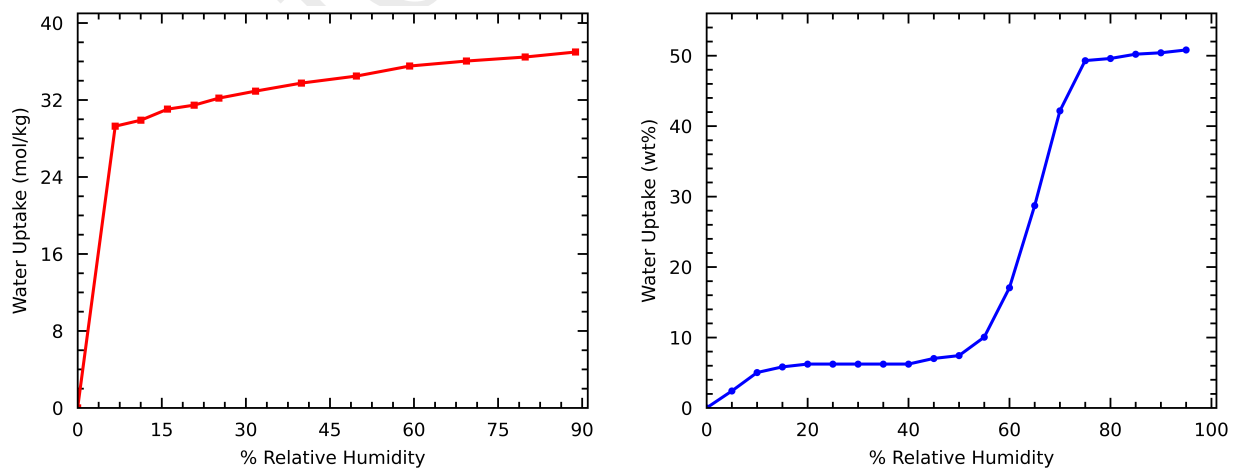


**Table 3.** Water uptake capacity of MOF-801 at varying conditions (Here,  $d_{gr}, mm$  = grain size,  $N$  = layer size,  $S/m, m^2/kg$  = surface to mass ratio,  $T_{ads}, ^\circ C$  = adsorption temperature and  $w, g/g$  = water uptake) [61]

$d_{gr}, mm$	$N$	$S/m, m^2/kg$	$T_{ads}, ^\circ C$	$w, g/g$
0.8 - 0.9	1	4.4	20	0.28
			25	0.26
			30	0.23
			35	0.18
0.4 - 0.5	1	8.8	20	0.26
			25	0.24
			30	0.21
			35	0.17
0.2 - 0.25	2	4.4	20	0.27
			25	0.25
			30	0.22
			35	0.19
0.2 - 0.25	1	17.8	20	0.23
			25	0.22
			30	0.20
			35	0.16

### Effect of humidity

Another crucial factor affecting the water adsorption capacity of a porous material is humidity. In 2012, Schoenecker et al. [63] looked into the effect of relative humidity (RH) in adsorption capacity of Mg-MOF-74 at 298 K and 1 bar pressure. The plot, Figure 2a, displays a steep initial uptake reaching approximately 30 mol/kg at low humidity. Beyond this, the uptake reaches about 37 mol/kg at ~90% RH. This behavior highlights the material's high affinity for water molecules across the full humidity range.



**Figure 2.** a) Water adsorption isotherms of a) Mg-MOF-74 at 298 K and 1 bar [63], and b) Y-shp-MOF-5, after activating sample at 298 K [64].

Similarly, AbdulHalim et al. (2017) [64], studied a hybrid microporous highly connected rare-earth-

based MOF named Y-shp-MOF-5 for autonomous indoor moisture control and observed that the RH vs water uptake plot produced an unusual sigmoidal profile, as in Figure 2b. The profile has a modest water uptake ( $\sim 5$  wt%) at low humidity ( $< 20\%$ ) indicating strong interaction between water molecules and open metal sites of the MOF. This is followed by plateau until  $\sim 55\%$  RH beyond which a sharp increase in uptake is observed, reaching  $\sim 50$  wt% uptake at  $\text{RH} > 85\%$ .

## VI. Conclusion and Outlook

As the global demand for clean water grows, finding sustainable ways to harvest water from the atmosphere has become increasingly important. Among the various materials studied for this purpose, Metal-Organic Frameworks (MOFs) stand out because of their high surface area and customizable structure. This review looked at several important factors that affect how well MOFs can adsorb water. For instance, MOFs with larger pores generally allow more water vapor to enter, leading to higher adsorption, while smaller pores may help retain water more strongly through capillary effects. Structural defects can sometimes boost water uptake by providing extra sites for adsorption, though too many defects might weaken the material. Similarly, making the surface of a MOF more hydrophilic tends to increase water adsorption, while hydrophobic surfaces may reduce it but help the material last longer in humid environments. The type of metal used in the framework also plays a role by affecting how water molecules interact with the structure. Environmental factors like humidity and temperature matter as well—higher humidity and lower temperatures usually lead to greater water uptake. Understanding how all these factors influence performance is key to designing MOFs that are both efficient and reliable for atmospheric water harvesting.

Despite these advancements, several research gaps remain. Future studies should focus on the development of MOFs that can maintain high water uptake at extremely low RH ( $< 20\%$ ) and across variable temperature ranges. Moreover, improving the regeneration efficiency and exploring scalable, eco-friendly synthesis methods are essential for real-world deployment. Integrating computational simulations with experimental work could also accelerate the discovery of high-performance MOFs tailored for diverse climatic conditions.

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