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Review

Evaluation of Metal–Organic Frameworks as Potential Adsorbents for Solar Cooling Applications

Muhammad Mujahid Rafique [1,2]

[1] Department of Mechanical Engineering, KFUPM, Dhahran 31261, Saudi Arabia; mujahidrafique89@gmail.com

[2] Faculty of Mechanical Engineering, TU Freiberg 09599, Germany

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Abstract: The reduction of carbon dioxide emissions has become a need of the day to overcome different environmental issues and challenges. The use of alternative and renewable-based technologies is one of the options to achieve the target of sustainable development through the reduction of these harmful emissions. Among different technologies thermally activated cooling systems are one which can reduce the harmful emissions caused by conventional heating, ventilation, and air conditioning technology. Thermal cooling systems utilize different porous materials and work on a reversible adsorption/desorption cycle. Different advancements have been made for this technology but still a lot of work should be done to replace conventional systems with this newly developed technology. High adsorption capacity and lower input heat are two major requirements for efficient thermally driven cooling technologies. In this regard, it is a need of the day to develop novel adsorbents with high sorption capacity and low regeneration temperature. Due to tunable topologies and a highly porous nature, the hybrid porous crystalline materials known as metal–organic frameworks (MOFs) are a great inspiration for thermally driven adsorption-based cooling applications. Keeping all the above-mentioned aspects in mind, this paper presents a comprehensive overview of the potential use of MOFs as adsorbent material for adsorption and desiccant cooling technologies. A detailed overview of MOFs, their structure, and their stability are presented. This review will be helpful for the research community to have updated research progress in MOFs and their potential use for adsorption-based cooling systems.

Keywords: MOFs; thermal cooling; sustainable developments; solar energy

1. Introduction

Energy consumption across different sectors is increasing continuously with households as the major contributor which is responsible for one-third of the world's total energy consumption [1]. The major portion of the energy in the household and almost 30% of the world's total energy is consumed by heating, ventilation, and air conditioning (HVAC) equipment [2,3]. Furthermore, the energy demands for heating and cooling applications are increasing at a rapid rate and are accounting for more than 17% of worldwide consumption as can be observed from Figure 1 [4]. This demand is projected to increase at a rapid rate in the future as well. To combat this increasing demand for energy, a target of 20% reduction in primary energy use by 2020 has been set by EU-28 countries [5] and to achieve this milestone different alternative energy technology needs to be introduced.

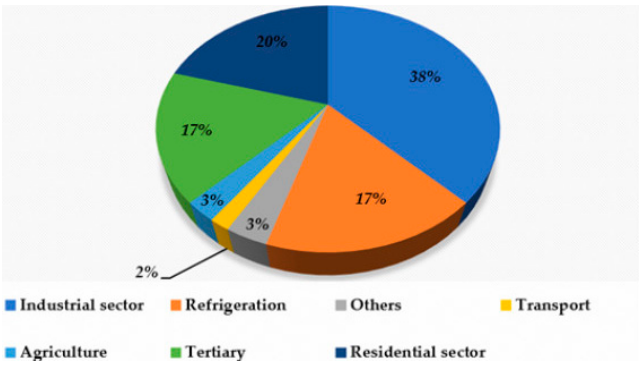


Figure 1. Consumptions of global energy in different sectors [5].

Different technologies and alternative cooling systems based on thermal energy including absorption, adsorption, and desiccant cooling have been investigated in recent years. The basic operating principle of a thermal cooling system is shown in Figure 2 [6]. These technologies are based on the process of dehumidification and cooling. Some adsorbent materials are used in these systems which have the potential to adsorb/absorb water molecules. Due to the thermally operated nature, the input energy is provided in the form of heat for the continuous operation of these systems. This makes the use of low-grade thermal energy sources such as solar, biomass, waste, etc., more feasible.

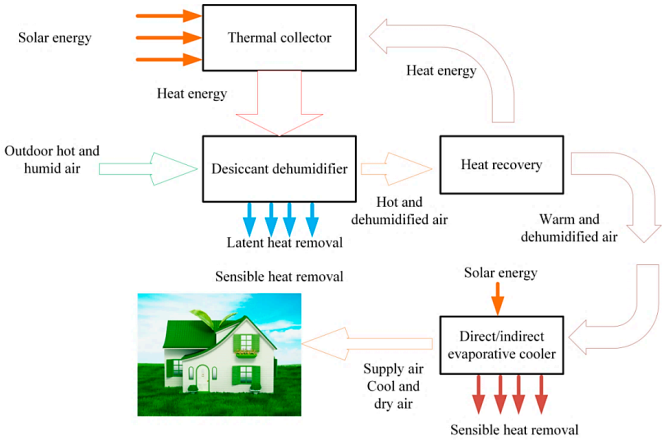


Figure 2. Thermally activated cooling system's working principle [4].

While thermally activated cooling systems offer advantages in terms of energy consumption and CO_2 emissions [7,8], despite the advantages offered by thermally driven cooling systems, it is observed that these systems are comprised of large components which make them bulky and expensive. Furthermore, most of the adsorbent used for these systems has larger water uptake capacity at higher partial pressure. Hence, it is very difficult to implement these technologies on a commercial and larger scale. These systems are available commercially but only at a small scale and only a few are installed for large scale applications [9].

Adsorption and desiccant cooling technology can be used as a great means of general cooling but, due to the above-mentioned issues, these systems have a lower coefficient of performance (COP) as shown in Figure 3 [10]. The average COP of these systems is less than 1. This lower value of COP and the bulky nature of these systems are a big hurdle for its development and implementation. Concerning this, different advancements are required for adsorbent materials used for these technologies to lower their weight, cost, and required temperature of regeneration.

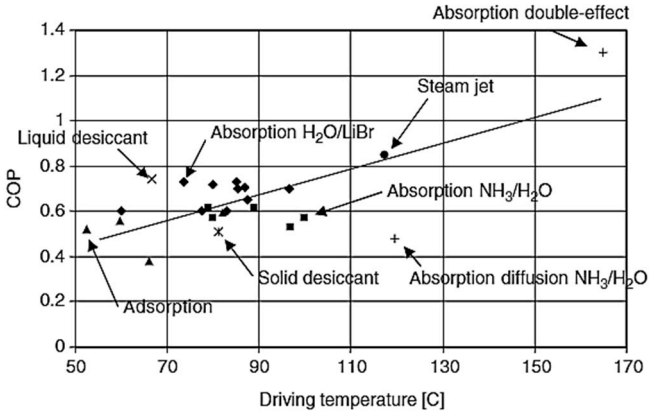


Figure 3. Coefficient of performance (COP) as a function of temperature [10]. Reprinted with permission from [10]. Copyright from 2007 Elsevier.

Metal–organic frameworks (MOFs) are a newly developed class of crystalline materials with highly porous structure and high adsorption capacity. These materials offer a wide variety of choices for its development because of individual choices of linker and metal-ligand according to the required structure and application. These materials have a high surface area which means that a small quantity of these materials can replace the bulk quantity of other porous materials for a particular application. The MOF materials are widely used for gas storage and filtration processes nowadays. In recent years, these materials have made great scientific advances due to the above-mentioned advantages.

Keeping all aspects in mind, the main aim of this research work is to present a comprehensive overview of MOFs for their potential use as adsorbents for thermally activated cooling technologies. The brief introduction of adsorption-based cooling and desired behavior of adsorbent material for cooling applications is described. The paper provides a comprehensive overview of MOF-based cooling and its future developments. Furthermore, comparative studies related to MOFs and other adsorbent materials commonly used for cooling applications are reviewed. The comprehensive plan to achieve the objectives of this research can be summarized as:

- Description of alternative cooling technologies that are both energy efficient and environmentally friendly.
- Research on thermal cooling systems for their development and promotion.
- A detailed review of available advanced adsorbent materials that can be employed for adsorption based solar cooling.
- Introduction to MOFs as an alternative to other adsorbents.
- The recent development of MOFs and their adsorption characteristics.
- Future needs for development and advancements of MOF-based cooling technology.

It is predicted that the use of MOF materials for both adsorption-based cooling technology will help for their development and promotion on a commercial scale. A suitable MOF can be selected based on the desired outcome and further tuned if needed. The use of these novel structures as an adsorbent for adsorbent-based cooling may perform better as compared to other materials that are widely used for these applications. In short, to find out this potential through a comprehensive review of adsorbent-based cooling systems, desired adsorbent behavior for these technologies and comparative adsorption properties of MOFs is the aim of this paper.

2. Thermally Activated Cooling Systems

The use of thermal energy for heating and cooling applications is one of the feasible options for the effective utilization of renewable energy sources such as solar, waste heat, biomass, etc. [11,12]. This can help to reduce the dependence on fossil fuels and to achieve the goals of sustainable development.

The naturally available energy sources can be used to drive thermally activated cooling systems such as adsorption [13,14] and desiccant cooling [4]. Apart from that, absorption cooling is also an option that can make use of these low-grade energy sources effectively [15]. A classification of thermally activated cooling is presented in Figure 4.

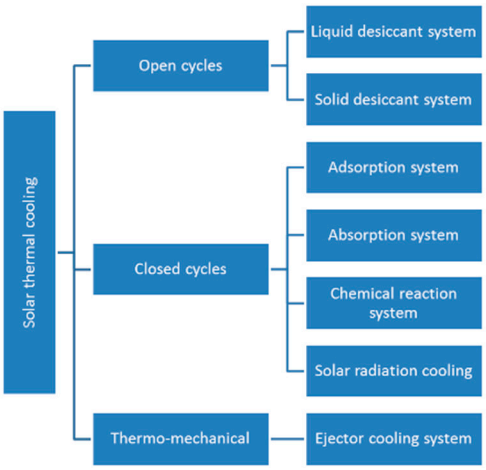


Figure 4. Classifications of thermally activated cooling.

The working of thermally activated cooling technology is based on two processes, which are adsorption and regeneration as illustrated in Figure 5. During the process of adsorption, process air is passed through a dehumidification unit composed of some adsorbent material. The adsorbent material adsorbs the moisture from the process air depending upon its adsorption capacity. The adsorbed moisture by the adsorbent material is removed during the regeneration process. Thermal energy, depending upon the required regeneration temperature is provided during this step. In this way, the process of adsorption and desorption continues in a cyclic loop [16].

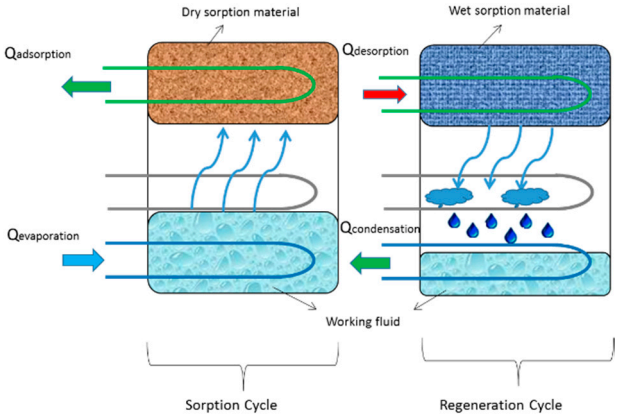


Figure 5. Two-step process of thermally activated cooling.

Thermally driven cooling technology provides many advantages over conventional HVAC devices which are based on the vapor compression cycle [17]. The direct use of thermal energy and low heat of regeneration are some of the advantages offered by this technology [18–20]. A summary of the potential advantages offered by this technology is summarized in Figure 6. Silica gel is widely used as adsorbent material for different cooling applications [21–23] such as trigeneration [24,25], air conditioning for automotive [26], and solar cooling [27,28]. However, adsorption at higher pressure is one of the major problems of silica gel utilization as adsorbent. This means that water adsorbed/desorbed by silica gel will be a part of its total adsorption capacity at lower pressure or normal operating conditions of the cycle. This will result in a large amount of adsorbent material required to achieve the desired

output and bulky systems having high capital cost [29–31]. Therefore, new and advanced adsorbent materials are required which can exhibit better properties according to the system requirements. The performance improvement of these systems is the only way forward for the development and promotion of this technology.

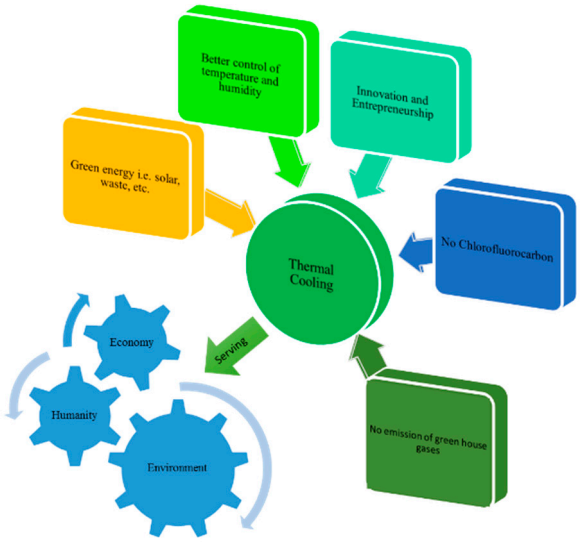


Figure 6. Advantages of thermal cooling technology.

3. Physical Adsorbents and Desired Adsorption Behavior

The adsorption process is categorized as physical and chemical adsorption and for adsorption-based cooling; the phenomenon of physical adsorption takes place [32]. The materials used for physical adsorption are known as physical adsorbents. The ideal adsorbents should have a higher enthalpy of adsorption, high porosity, large surface area, and high uptake capacity [33,34].

Regardless of the type of adsorbent, material with high uptake at lower partial pressure, and having stepwise isotherm is preferred as this will give better efficiency and performance [35,36]. Furthermore, the phenomenon of hysteresis is undesired for the adsorption process as this will cause a loss of inefficiency. Many researchers have used silica gel [37,38], zeolite [39,40], and functional adsorbent material such as FAM Z05 [41], Z01 [42], Z02 [43], and [44] for different applications. All these adsorbents show good adsorption characteristics, especially silica gel and zeolites. It is found that the use of zeolite in natural gas-driven heat pumps can reduce the energy requirements of a conventional household boiler by up to 30% [40].

Activated carbon (AC) is an effective adsorbent which has a surface area of 500–1500 m^2/g [45] and it can adsorb refrigerants such as R134a, ammonia, ethanol, and methanol with a high uptake rate [46–48]. AC has a low adsorption heat (1800–2000 kJ/kg) and poor thermal conductivity (0.4 W/(m· K)) [49]. The surface area of silica gel is 100 to 1000 m^2/g and it has a regeneration temperature of 50–120 °C depending on its type. It has large adsorption capacity, low mass transfer, and large adsorption heat of 2500–2800 kJ/kg. Low mass transfer is not a desirable phenomenon for thermally activated cooling systems. The zeolites have a high adsorption heat (3000–4500 kJ/kg) and poor thermal conductivity (0.2 W/(m·K)) which reduces its heat transfer performance [50,51]. Zeolites can be regenerated at a temperature of 200–300 °C which is not desirable for cooling applications. The porosity and surface area of commercially used adsorbents along with their potential applications are presented in Table 1.

Table 1. Properties of commonly used adsorbents and their potential uses.

Adsorbent	Properties	Potential Applications
Activated Carbon	Surface area: 500–1500 m^2/g Porosity: 0.3–1.5 cm^3/g	Organic removal Separation of air Purification of gases
Activated Alumina	Surface area: 300–400 m^2/g Porosity: 0.25 cm^3/g	Air separation Gas purification
Silica Gel	Surface area: 100–1000 m^2/g Porosity: 0.4–1.2 cm^3/g	Desiccant HVAC systems Humidity control of air
Molecular Sieves (Zeolites)	Surface area: 2800–3500 m^2/g Porosity: 1.4–2 cm^3/g	Deodorization of air Gas masks Wastewater purification Storage material

4. MOF-Based Adsorption Cooling

MOFs are novel crystalline porous materials with high porosity, flexible structure, and high adsorption capacity. The basic structure of an MOF is shown in Figure 7 [52]. A typical MOF material consists of an organic linker and a metal ion. The choice of metal ion and organic linker offers a great variety of flexibility for different applications. The combination of metal ion and organic linker can be chosen depending upon the gases and how much is to be adsorbed/absorbed. These materials can have great heat and mass transfer potential depending upon the choice of structure. The associated properties of MOFs offer a broader look and possibility of developing the MOF-based cooling system.

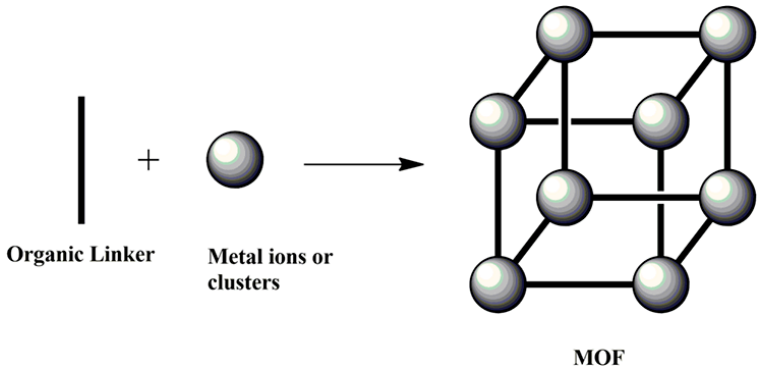


Figure 7. Basic structure of a metal–organic framework (MOF) [52].

MOFs have recently attracted great interest in the gas storage sector, but there have been some reports of aspiring cooling applications. The potential use of MOFs for cooling applications needs to be explored because of their high mass loading capacity and relatively low heats of adsorption. They could prove to be an excellent adsorbent for adsorption chillers and desiccant dehumidifiers. The wide variety of topologies, the high scope of porosity and surface area [53,54], and post/pre-synthesis functionalization possibilities [55–59] make MOFs suitable for a wide variety of applications such as storage [60,61], adsorption and separation [62–65], and catalysis [66–69].

Computational studies have shown that the use of an MOF in adsorption chillers can help to achieve a coefficient of performance greater than one [70]. This is a great achievement because these systems always had a COP value of less than one. Only limited work is available for MOF-based cooling such as that of Henninger et al. [71], who depicted the potential use of MOFs in adsorption technology. The instability of MOFs is a hurdle for their use as an adsorbent for cooling applications but, to date, many stable MOFs have been developed. Many MOFs are less stable toward water [72–75] but more stable towards methanol, ethanol, and ammonia [76]. That is why the choice of a suitable MOF material should also consider the nature of the working fluid.

De Lange et al. [77] tested 18 different MOFs in combination with either methanol or ethanol as a working pair for their potential applications in heat pumps. The results showed that thermodynamically CAU-3, UiO-67, and ZIF-8 can be employed with both methanol and ethanol but UiO-67 will show some instability during the operation. CAU-3 and ZIF-8 will be more effective and stable for utilization in adsorption chillers with both methanol and ethanol.

Motkuri et al. [78] observed and reported the behavior of microporous and mesoporous MOFs for their adsorption capacity. The saturation uptake capacity for microporous MOFs at low saturation pressure ($P/P_o = 0.02$) is observed to be greater than 4 mmol g^{-1}. In contrast, an uptake capacity of greater than 14 mmol g^{-1} is observed for mesoporous MOFs at a P/P_o of 0.4. It can be concluded that, depending upon the required water uptake, the desired framework of material can be employed which can be very advantageous for adsorption-based cooling applications [79–82].

The specific pore volume and surface area of MOFs strongly affect their water adsorption properties for adsorption or desiccant cooling. MIL-100(Cr) and MIL-101(Cr) have been identified to possess large water adsorption quantity and exceptional hydrothermal stability by numerous researchers, as can be observed from Figure 8 [83]. The high adsorption uptake makes these MOFs a feasible adsorbent for adsorption-based cooling systems. Better adsorption characteristics, lower required heat, and stable nature have increased the interest of these materials to be used as adsorbents for cooling applications.

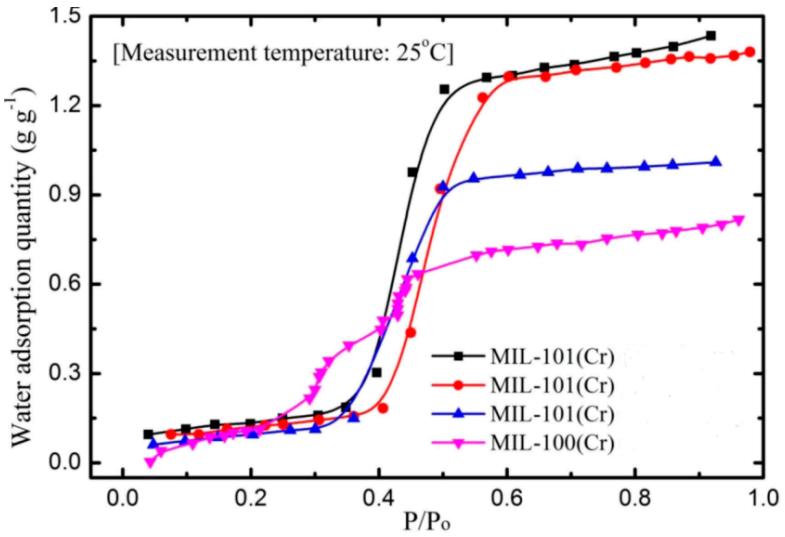


Figure 8. Adsorption isotherms of MIL-101(Cr) and MIL-100(Cr) compounds [83].

5. Historical Background of MOFs as Adsorbents

Aristov [84] in the year 2007 initially suggested the idea of MOF-based heat pumps and since then several MOFs had been studied and investigated for their adsorption and water uptake capabilities. Cu-BTC, MIL-101Cr, and CPO-27 are some of the widely researched MOFs for their potential use as adsorbent materials. The structural details of Cu-BTC (HUST-1) can be found in references [85,86]. The process of water adsorption and uptake capacity of MOF materials are investigated by [87,88]. The water uptake capacity of CU-BTC was found to be 6% by weight at 22 °C and 2.7 mbar. Rezk et al. [15] concluded that, among different MOFs, the water uptake capacity of Cu-BTC and FeBTC is found to be the highest. This large uptake capacity is because of their high porosity and surface area. In another study related to Cu-BTC, Gul-E-Noor et al. [87] showed that the Cu-BTC network can be decomposed because of the presence of water in its structure.

The adsorption characteristics of MIL-101Cr have been investigated widely [14,89]. Ehrenmann et al. [89] found that MIL-101Cr has a high-water uptake capacity at low operating pressure and there will be only a slight decrease in its adsorption capacity over time. Rezk et al. [14,15] concluded that, with ethanol as a working pair, the adsorption behavior of MIL-101Cr is better as compared to MIL-100Cr, MIL-53Cr,

CPO-27Ni, Cu-BTC, and Fe-BTC. The results also showed that MIL-101Cr is stable after 20 cycles at 25 °C. CPO-27 (MOF-74) is another MOF family which is attractive for use in adsorption applications. CPO-27 has four types: CPO-27Zn [90], CPO-27Co [91], CPO-27Ni [92], and CPO-27Mg [93]. Glover et al. [93] stated that all these four types of CPO-27 show a competitive water adsorption behavior. A summary of three main MOFs which can be potentially employed for adsorption-based cooling application is presented in Table 2.

Table 2. Characteristics of CU-BTC, MIL-101Cr, and CPO-27.

Name of MOF	Water Uptake Capacity	Remarks
CU-BTC	6% by weight 0.324 kg_{ref}/kg_{ads}	Not stable
MIL-101Cr	1.01 kg_{ref}/kg_{ads} 0.3 kg_{ref}/kg_{ads}	Stable
CPO-27	0.1 to 0.5 kg_{ref}/kg_{ads}	-

A comparative numerical analysis carried out by Bareschino et al. [94] showed that the desiccant wheel emended with MIL101@GO-6 (MILGO) has performed better in comparison to conventionally available silica gel-based desiccant wheels. Kuesgens et al. [95] tested several MOF materials and concluded that MIL-101 (Cr) has promising characteristics for use in adsorption-based cooling. Similarly, Khutia et al. [96] found that MIL-101 (Cr) has a high water uptake capacity which is desirable for their use in adsorption chillers. Yan et al. [97] employed the MIL-101 (Cr) structure and developed a novel structure, MIL101@GO-6, which has a water uptake capacity sic times higher than silica gel's. Moreover, other different MOFs have also been investigated for their potential use in adsorption-based applications such as ISE-1 [98], 3D pillared-layer [99], MOF-5 [100], MOF-177 [100], copper-based MOF [101], MOF-801 [102], and MOF-841 [102].

Tannert et al. [103] reported desirable water uptake characteristics and thermal stability of that Al-based metal–organic framework MIL-53(Al)-TDC which has an average heat of adsorption of only 2.6 kJ g^{-1}. This indicates the low heat requirement of these MOFs which can be provided by the residual heat from the condenser [104]. In another study, Brandt et al. [105] concluded that MOF-177, NH2-MIL-125(Ti), and MIL-160 show excellent adsorption characteristics and they are stable under both humid and dry conditions. Shi et al. [106] also highlighted the use of MOFs to achieve higher COP of adsorption-based cooling and identified the 10 best MOFs.

MOFs have the potential to be ideal adsorbent materials for this application, as they can be tuned to have desired adsorption behavior for different refrigerants. Different MOFs have also shown good characteristics for adsorption of water, methane, or other gases. Wu et al. [107] designed 424 types of tetrazolated-based MOFs and selected Zr-fcu-MOF-2Py material with the highest methane adsorption capacity. Li et al. [108,109] identified 15 MOFs with good adsorption performance of CO_2 in the presence of H_2O from 5109 computational ready experimental metal–organic frameworks (CoRE-MOFs). Erdos et al. [110] identified six MOFs that could satisfy the high-efficiency adsorbents in adsorption heat pumps. Chen et al. [111] found zirconium-based MOFs to be a suitable adsorbent for cooling applications. Xia et a. [112] concluded from their theoretical model that the use of COF-5 MOF enables adsorption-driven heat pumps to operate with a high coefficient of performance. UiO-66 has also been reported to be a promising adsorbent for cooling applications due to the high specific cooling effect [113,114].

6. Comparison of MOFs with Other Adsorbents

Figure 9 provides a comparison of conventional adsorbents and MOFs in terms of their surface area and pore volume [4]. In general, MOFs showed exceptionally high porosity, well-defined molecular adsorption sites, and a large surface area (up to 5500 m^2/g) in comparison to currently used adsorbents like silica gel (1000 m^2/g), zeolite (900 m^2/g), and activated carbon (1300 m^2/g), which suffer from low water uptake. The HKUST-1 has 93.2% better uptake as compared to silica gel RD-2060. This is

due to the higher surface area of HKUST-1 as can also be observed from Figure 10 [115]. This could lead to a considerable increase in refrigerant flow rate, cooling capacity, and/or reduction of the size of the adsorption cooling system. This also highlights that the use of MOFs will improve the efficiency of adsorption-based cooling systems. It can also be noted that the advanced MOFs are being investigated with time which is providing a possibility to increase the thermal performance of thermal cooling technologies.

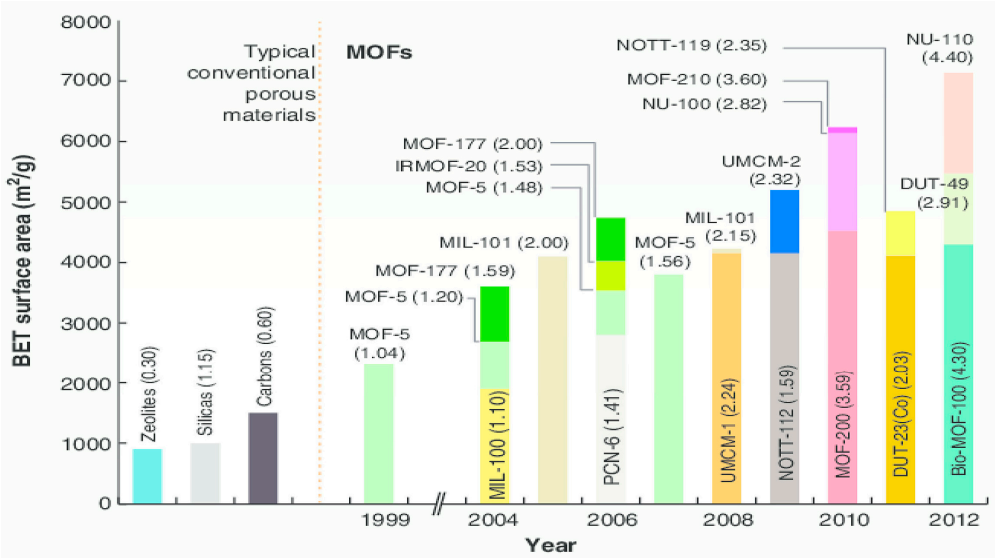


Figure 9. Comparison of conventional adsorbents and MOFs [4].

Property	HKUST-1	MIL-100	Silica gel RD-2060
Chemical Formula	$C_{18}H_6Cu_3O_{12}$	$C_9H_3FeO_6$	SiO_2
Granules size	16 µm	5 µm	0.18–1 mm
BET surface area	1500–2100 m^2/g	1300–1600 m^2/g	840 m^2/g
Bulk density	0.35 g/cm^3	0.16–0.35 g/cm^3	1 g/cm^3

Figure 10. Physical properties of three different MOFs [115].

The ratio between water uptake at equilibrium and maximum water uptake capacity concerning partial pressure for three materials shows that HKUST-1 is more effective than silica gel RD-2060 in adsorbing water vapors closer to its maximum water uptake, in particular at low partial pressure values [115]. Figure 11 reports the comparison between dehumidification efficiency (η_{deh}) predicted by the model developed by Bareschino et al. [94] for silica gel and MILGO (MIL101@GO-6)-based desiccant wheel. The simulations were carried in the same operating conditions for both desiccant wheels. It can be observed that a MILGO-based desiccant wheel has better dehumidification performance as compared to the silica gel desiccant wheel.

The water adsorption isotherms of conventional adsorbents and MOFs are presented in Figures 12 and 13, respectively [4]. It can be noticed from the adsorption isotherms that the water uptake performance of MOFs is better with MIL-101(Cr) showing the highest capacity to adsorb water vapors.

The type of isotherm further reveals that the MIL group of MOFs are more suitable for applications at high relative pressure [116], while CPO will be better at a low relative pressure range [117–119].

The enthalpy of adsorption which is the heat released during the process of adsorption is crucial for the selection of an adsorbent as it determines the heat required for regeneration. This directly influences the efficiency of an adsorption cooling or heating system; the lower the adsorption heat of a material, the less energy will be required to regenerate the material and the higher the efficiency will be. The calculated enthalpy of adsorption for different MOF materials is presented in Figure 14 [77]. The CAU family of MOFs has the enthalpy of adsorption in the range of 44–52 kJ/mol, whereas the MIL group has it in the range of 40–72 kJ/mol. The value of adsorption enthalpy for the UiO group of MOFs is found to be between 48 and 53 kJ/mol. In general, most of the MOFs have a lower enthalpy of adsorption in comparison to conventional adsorbent materials. This further indicates that the MOF materials have the potential to increase the efficiency of adsorption-based cooling technologies due to the lower requirement of energy for the regeneration process [77].

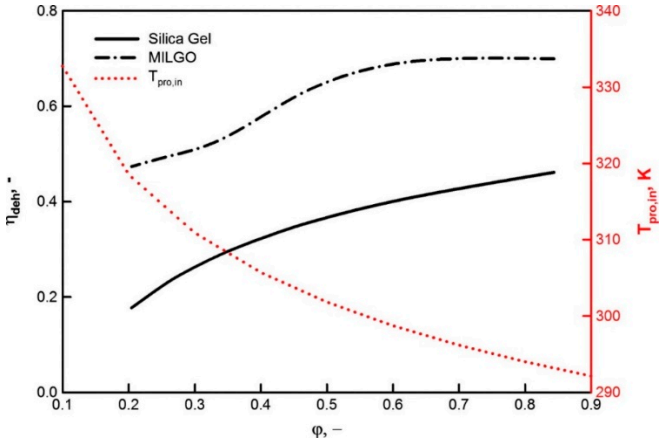


Figure 11. Comparison between dehumidification efficiency (η_{deh}) for a MIL101@GO-6 (MILGO) and a silica gel-based desiccant wheel as a function of the relative humidity (φ) of process air [94]. Reprinted with permission from [94]. Copyright 2017 Elsevier.

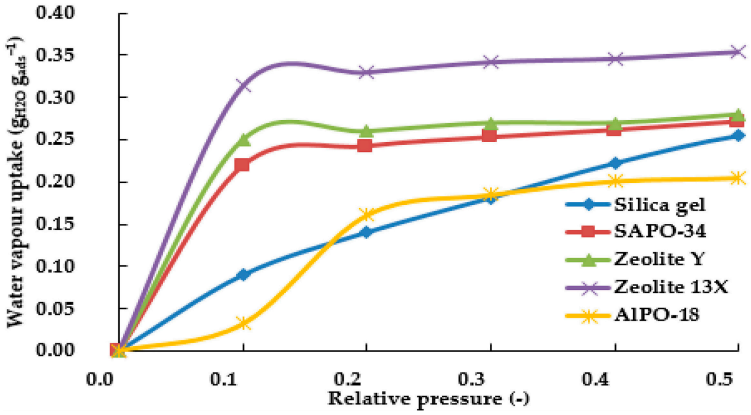


Figure 12. Water adsorption isotherms of conventional adsorbents at 25 °C [4].

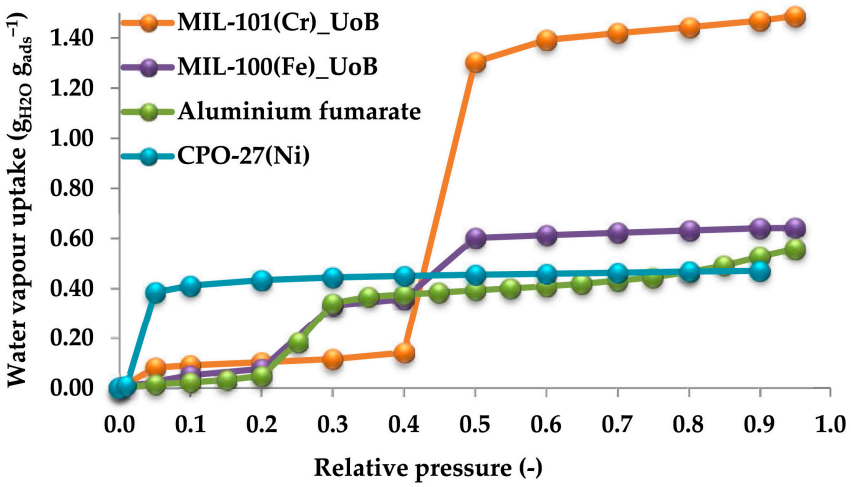


Figure 13. Water adsorption isotherm of MOFs at 25 °C [4].

Material	Enthalpy of adsorption (kJ/mol)
CAU-1	52
CAU-1-$(OH)_2$	48
CAU-3	48
CAU-3-NH_2	44
CAU-8	-
CAU-10-H	52
Al-fumarate	52
MIL-53	51
MIL-53-NH_2	52
MIL-125	45
MIL-125-NH_2	40
MIL-100	72
MIL-101	43
MIL-140A	44
MIL-140C	47
UiO-66	53
UiO-67	48
ZIF-8	45

Figure 14. Average enthalpy of adsorption of different MOFs [77]. Reprinted with permission from [77]. Copyright 2015 ACS Publication.

Apart from the above-mentioned studies, a few reviews involving related topics of CO_2 capture with MOFs have appeared very recently [120–124]. Demirocak et al. [125] also compared the performance of HKUST-1 with zeolite for cooling applications using the TRNSYS model. The MOF adsorbent for solar adsorption refrigeration is a nanocomposite made from an MOF matrix with carbon nanotubes incorporated therein and is preferably used as a powder [126,127]. A comparison of different adsorbent materials including MOFs is presented in Table 3 [128]. It can be observed that MIL 101(Cr)-H_2O has a better water uptake capacity and it can be regenerated at a temperature of 90 to 140 °C. The temperature required for the regeneration of SAPO 34-H_2O is also below 100 °C. The higher uptake capacity and lower requirement of regeneration temperature is an indication that MOFs can be a suitable material for adsorption cooling.

Table 3. Characteristics comparison of adsorbent materials [128].

Working Pair	Working Pressure	Working Temperature (°C)	Uptake Capacity (kg_{ref}/kg_{ads})	Is Refrigerant Thermally Stable?	Is Refrigerant Toxic?	Is Refrigerant Flammable?
Activated carbon-NH_3	Positive	80 to 200	0.29	Yes	Yes	Yes
Activated carbon-Methanol	Vacuum	80 to 100	0.45	No	Yes	Yes
Activated carbon-Ethanol	Vacuum	80 to 120	0.19	Yes	Yes	Yes
Silica gel-H_2O	Vacuum	50 to 120	0.30	Yes	No	No
Zeolite-H_2O	Vacuum	200 to 300	0.17	Yes	No	No
SAPO 34-H_2O	Vacuum	80 to 90	0.29	Yes	No	No
MIL 101(Cr)-H_2O	Vacuum	90 to 140	1	Yes	No	No

7. The Future of MOF-Based Adsorption Cooling

While maximum adsorption capacity of silica gel is good, the working pair of silica gel and water shows a low hydrophilic characteristic and has lower water uptake, especially at lower partial pressure. The limitations of available adsorbent materials arise in the need for the development of alternative materials with higher adsorption capacity, lower regeneration temperature, and stable nature at high temperatures. The above-mentioned literature shows that MOF materials can prove to be a good alternative to commercially available adsorbent materials for these cooling technologies.

Currently, more than 20,000 MOF structures are known due to the flexible and rich variety of topologies associated with these crystalline materials. The porosity and surface area of these materials is increasing with the development of each new structure. Apart from that, the associated properties of these materials can be tuned by pre- or post-methods according to the desired behavior.

The research for the use of MOFs for cooling applications is a topic of interest but is still at the initial stage. Water uptake capacity, regeneration temperature, and stability are the basic figure of merits for an MOF to be used for thermal cooling applications. New advancements are in progress to make these materials best fit for this technology but most of the developed MOFs still face issues of instability that need to be overcome. Most of the MOF compounds are synthesized at a lab-scale and only a few are available at commercial scale. These materials should be tested under real conditions to check their suitability for adsorption-based cooling. A summary of different adsorption and regeneration characteristics of MOF materials is presented in Figure 15. It can be observed that the MOF materials have a lower value of regeneration temperature and better sorption capacity, which are the positive attributes to be a good adsorbent for cooling applications. Despite promising sorption properties, the thermal stability of MOFs is still a challenge and only a few MOFs have been reported which are stable at higher temperatures. The effective use of these materials will allow the exploitation of yet mostly unused low-temperature heat sources of energy which will lower the use of carbon-emitting fuels.

MOFs	Surface Area (m^2 g^{-1})	Pore Volume (cm^3 g^{-1})	Sorption Capacity (g g^{-1})	Possible Regeneration Temperature (°C)
HKUST-1	1340	0.72	0.55	–
MIL-100(Fe)	1549	0.82	0.81	–
MIL-101(Cr)	3017	1.61	1.28	–
DUT-4	1360	0.79	0.28	–
ZIF	1255	0.64	0.02	–
MIL-100(F)	1517	–	0.68	80
MIL-100(Cl)	1522	–	0.60	80
MIL-100(SO_4)	1456	–	0.61	80
MIL-101(Cr)	2059	1.103	0.92	90
MIL-101(Cr)	–	–	1.43	90
MIL-101(Cr)	4150 ± 200	-	1.7	70
MIL-100(Fe)	2300 ± 100	–	0.9	70
MIL-100(Al)	1970	–	0.76	70
MIL-100(Cr)	1980	–	0.72	70
MIL-100(Al)	1814	1.14	0.52	140
MIL-100(Fe)	1917	1	0.75	140
MIL-101-H	3124	1.56	1.3	80
MIL-101-NH_2	2146	1.22	0.94	80
MIL-101-NO_2	2509	1.07	0.93	80
MIL-101-SO_3H	1920	0.92	0.68	80
Basolite™C300	1500–2100	–	0.65	140
Basolite™A100	1100–1500	–	0.21	140
Basolite™F300	1300–1600	–	0.33	140
Basolite™C300	1500–2100	–	0.46	85
Basolite™F300	1300–1600	–	0.37	85

Figure 15. Adsorption and regeneration characteristics of MOFs.

8. Concluding Remarks

Global energy consumption shows a continuous rise with households and buildings as major contributors to this increase. Due to improved living style and climatic changes, the demand for HVAC technology to provide indoor comfort conditions is increasing at a rapid rate. The reduction of energy consumption and the use of environment-friendly HVAC technology is a must to achieve low energy and sustainable goals. In this regard, adsorbent-based thermal cooling technology is a suitable alternative to conventional cooling systems. Adsorption-based cooling systems are available commercially and most of them use silica gel or zeolite as adsorbents because of their suitable adsorption characteristics. These systems currently face issues of lower performance and bulky nature. The development and promotion of these systems are directly related to their performance improvement. One way of achieving performance improvement is the development and utilization of new adsorbents such as MOFs. The MOF structures have recently received considerable interest due to their enhanced properties and structures. New concepts and reports have been published recently and successfully with the tools and promising applications for MOF. While the instability of MOFs could be a hurdle for their use as an adsorbent for cooling applications, to date many stable MOFs have been developed.

This paper describes the exploration and production of MOF-based cooling technologies. The central idea of this study is to highlight the potential use of MOFs for adsorption and desiccant cooling systems. The potential of MOFs as adsorbents in adsorption-driven cooling is thoroughly accessed. The main findings of this paper can be summarized as:

- Regardless of the type of adsorbent, a material with high uptake at lower partial pressure and having stepwise isotherm will be preferred for adsorption-based cooling applications. This type of adsorbent material will give better efficiency and performance.

- The adsorption-based cooling with conventional adsorbent material such as silica gel or zeolites normally have a COP value less than one but the simulation studies available in the literature showed that the use of MOF in these technologies can help to achieve a coefficient of performance greater than one.
- Better adsorption characteristics, lower required heat, and stable nature has increased the interest of these materials to be used as adsorbents for cooling applications. MIL-101Cr has a high water uptake capacity at low operating pressure and there will be only a slight decrease in its adsorption capacity over time.
- The results presented in the literature showed that HKUST-1 has 93.2% better uptake as compared to silica gel RD-2060. The high-water uptake capacity of HKUST-1 shows that it could be a suitable adsorbent material for adsorption-based cooling.
- Furthermore, the literature survey showed that Cu-BTC and CPO-27 are some of the other widely researched MOFs for their potential use as adsorbent materials for these applications.
- HKUST-1/water, MIL101/water, UiO-66/water, COF-5/ethanol and Maxsorb III/ethanol working pairs have the potential to increase the performance of adsorption cooling technologies.

While MOF materials have a huge potential for adsorption-based cooling technologies, additional research is required to develop the perfect models to accurately predict the performance of MOF-based cooling systems.

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