



Recent advances in adsorption heat transformation focusing on the development of adsorbent materials

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Adsorption heat transformation (AHT) is an environmentally friendly energy-saving process applied for air conditioning purposes, that is, either for cooling (including also ice making and refrigeration), or heating. AHT is based on the cycling adsorption and desorption of a working fluid in a porous material. When the working fluid is driven to evaporation by the active empty sorbent material, the required heat of evaporation translates into useful cooling in thermally driven adsorption chillers. Driving heat regenerates the empty sorbent material through desorption of the working fluid. The heat of adsorption in the sorbent material and the heat of condensation of the working fluid can be used in the adsorption heat-pumping mode. Thus, adsorption heat transformation contributes to energy-saving technologies. Adsorbent development plays a critical role for the improvement of AHT technologies. Besides silica gel and zeolites as adsorbent materials, which are up to now used in the commercially available AHT devices; especially metal-organic frameworks (MOFs) are getting more attentions in recent years. Composite materials from salts with silica gels, zeolites and MOFs as well as activated carbons have also been researched to contribute to AHT technologies. Reduction of installation/production cost and enhancement of the efficiency of AHT devices need to be achieved to increase the wider usage of AHT.

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Introduction

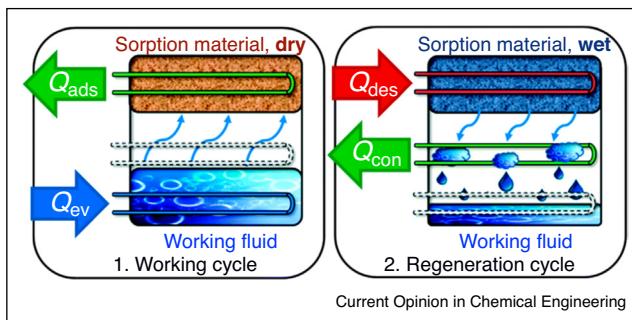
Increasing energy demand is one of the biggest issues for our civilizations and entails the search for alternative energy-saving technologies. Adsorption heat transformation (AHT) is a heating and cooling method, which belongs to present commercially available energy-saving and eco-friendly technologies; however, it requires further development for wider implementation. The advantages of AHT are eco-friendliness by avoiding halogenated refrigerants, silent operations by not using a compressor and the use of low temperature driving heat sources (solar, geothermal, industrial waste heat, etc.) for regeneration [1,2]. Disadvantages are large size [2,3], low efficiency, and high installation cost, and these aspects need to be improved for the development of AHT devices [4].

Working principle of AHT

AHT can be generally divided into closed and open operating systems. In the thermodynamic sense, ‘closed’ refers to a system with no exchange of matter but only the exchange of energy with the environment. Thus, also toxic working fluids such as methanol and ammonia can be used in such a closed system. In open AHT energy and matter are exchanged, for example, water vapor as an adsorbate is taken from and released to the environment. Furthermore, depending on the working conditions it is possible to use AHT either for cooling (including also ice making and refrigeration), or heating [5,6].

Adsorption-based heat transformation is a relatively old technology, which utilizes the thermodynamic principle to convert exothermic and endothermic processes into useable heating and cooling. The working principle of adsorption-based heat pumps and adsorption chillers is illustrated in Figure 1 [7]. During the adsorption and condensation process, heat is released as Q_{ads} and Q_{con} , which can be used for heating purposes. The liquid working fluid will be evaporated, during which heat is extracted as Q_{ev} from the environment performing the desired cooling [8,9].

The main benefit of adsorption heat transfer compared to conventional heating or compressor cooling systems is the utilization of waste heat for Q_{des} to drive the process in the regeneration step. In adsorption chillers, the heat of

Figure 1

The working principle of sorption-based heat transformation consists of two switchable chambers with one of them being in the working and the other in the regeneration cycle. In the working cycle, a liquid working fluid is evaporated (under reduced pressure for water). The required heat of evaporation (Q_{ev}) is taken from the environment and leads to utilizable cooling. Heat of adsorption (Q_{ads}) is released when the dry sorption material starts to adsorb the working fluid. At sufficient loading of the sorption material, the chamber is switched to the regeneration cycle where heat of desorption (Q_{des} , also termed heat of regeneration) (from solar, geothermal, industrial waste heat etc.) is used as driving heat to desorb the working fluid from sorption material. The working fluid is condensed in the regeneration cycle, whereby heat of condensation (Q_{con}) is released.

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desorption Q_{des} is essentially transformed into useful cold by regenerating the wet sorption material, so that heat of evaporation Q_{ev} can be utilized. In the adsorption heat pumping mode, Q_{ads} and Q_{con} are utilized and Q_{ev} presents the additional energy gain from the environment to Q_{des} (ideally $Q_{ads} + Q_{con} = Q_{des} + Q_{ev}$).

The demands on the adsorbent can be derived from the application. Since AHT is a cyclic application, the adsorbent has to show a high hydrothermal stability under applied temperatures over thousands of cycles. The temperature boundaries are defined by the setup of the device and the specific application. An overview of the most common heat sources and sinks are listed in **Table 1**. A typical application is for instance a heat pump setup using an earth probe, a floor heating system and a water-based hydraulic circuit delivering desorption temperatures at slightly below 100°C. The vapor pressures at these temperatures ($p_s(T)$) can be used to calculate the relative pressure for adsorption and desorption at which the process step takes place:

$$\left(\frac{p}{p_0}\right)_{ads} = \frac{p_s(T_{evap})}{p_s(T_{ads})}, \quad \left(\frac{p}{p_0}\right)_{des} = \frac{p_s(T_{cond})}{p_s(T_{des})}$$

For the described example, relative pressure is 0.22 for adsorption and 0.07 for desorption, respectively.

Table 1**Overview of temperature boundaries for AHT**

	Application	Heat source	Temperature
Low temperature source	Heating	Earth probe	10°C
	Heating	Ambient air	-10 to 15°C
	Cooling	Ambience	-10 to 20°C
Mid temperature	Heating	Floor heating	35°C
	Heating	Radiator	60°C
	Cooling	Ambience	35°C
Desorption temperature		Waste heat	55–100°C
		Gas burner	>100°C

An adsorbent material should fulfill the following requirements in order to be suitable for AHT: (i) The sorption isotherm should have an S-shape (IUPAC classification Type V [10]) with a steep rise in the relative pressure range of $p/p_0 \approx 0.1\text{--}0.3$ for an effective profitable uptake in the adsorbent material [11]. The pressure range can vary depending on the desired working conditions described above. Additionally, no hysteresis is desired which reduces the usable part of the loading and causes loss of sensible heat [12,13]. The noted S-shape is advantageous because it enables a large lift of adsorption within a narrow relative pressure range [14]. (ii) The uptake or working capacity should be higher than 0.2 g/g [12], yet, for application, materials are better compared on capacity per unit volume, either a g/mL, mL/mL or kWh/m³ [9]. The desired S-shape requirement is, however, not fulfilled by the water vapor sorption isotherm of silica gel. Despite its linear water sorption isotherm silica gel is often used in commercially available AHTs due to its comparably low price. However, adsorbents with linear water sorption require a broader temperature range to achieve a similar power output when compared with an adsorbent with S-shape sorption. (iii) Very essential is that the adsorbent is hydrothermally stable to over the desired 10-year or higher lifetime of the device, which amounts to over 100 000 adsorption–desorption cycles. (iv) Fast sorption kinetics and sufficient thermal conductivity for Q_{ads} and Q_{des} heat dissipation are also important properties, but these properties mostly rely on the whole system consisting of the adsorbent itself, eventually a binding agent, the heat transfer structure, the hydraulic circuits, the evaporator/condenser structure and so on. Especially, the form of the adsorbent and contact to the heat transfer structure are of main influence [15]. (v) Reasonable production costs of the adsorbent must be also considered for real life applications. Unfortunately, the production cost for MOFs as adsorbents are difficult to quantify in the view of the still low-scale production of many MOFs for research purposes. Such an analysis was done in the techno-economic analysis of four MOFs with possible use for natural gas storage, but not suitable for AHT, ending up with costs of around \$13/kg–\$36/kg [16]. First life-cycle assessment (LCA) calculations of two MOFs, namely CAU-10 and Alfum, revealed a higher GWP

(global warming potential) and PENR (non-renewable primary energy demand) as compared to the also reported state-of-the-art materials zeolite 13X and silica gel. However, the number of cycles until brake-even will be reached is lower in case of the MOFs since these materials need either a lower desorption temperature (as compared to zeolite) or less material (as compared to silica gel) [17].

An important indicator for the energetic efficiency of the adsorption heat pump cycle is the so-called coefficient of performance (COP). This is determined as useful energy output divided by the required energy as input [9]. Below is the calculation of COP for heating (COP_H) and for cooling (COP_C) given as

$$COP_H = \frac{-(Q_{con} + Q_{ads})}{Q_{des}}, \quad COP_C = \frac{Q_{ev}}{Q_{des}}$$

The COP_C values range from zero to one and COP_H range from one to two [9]. For instance, in the screening work involving the adsorbents zeolites, silica gel, active carbon, composites and MOF materials for different adsorbates (water, methanol, ethanol, ammonia, acetone, benzene and *n*-butane) the COP_C value ranges from 0 to 0.6 with the COP_H value ranging from 1.0 to 1.2. The cycling operating conditions were given for cooling mode as 50°C (adsorption temperature), 50°C (condenser temperature), 5°C (evaporator temperature) and for heating mode 50°C (adsorption temperature), 50°C (condenser temperature), -23°C (evaporator temperature) [18**]. It is important to consider that the COP values vary with the working conditions. Working conditions depend also on the sorption properties of the adsorbent–adsorbate working pairs, which is demonstrated in Figures 3 and 4. Above mentioned working conditions were selected to demonstrate stringent conditions from the American Heating and Refrigeration Institute [18**].

It is difficult to compare conventional compressor cooling systems with AHT with respect to power density, which depends on the conditions and on the size of the systems. Energy storage capacity could also be taken into account for compression coolers but it is given for AHT based systems not for vapor compression systems. A sensible comparison to compression could be done by considering primary COP (PCOP), which is given for example for cooling as PCOP_C (defined as the ratio of heat removed from the system to the total primary energy consumed), and which can be used to compare with AHT. Primary COP_C is given for typical air conditioners to less than one. The refrigeration system based on the MOF UiO-66 has PCOP_C of 0.85, which is comparable with commercial vapor compression cooling systems [19].

This minireview focuses on very recent developments and research interests in the field of AHT, especially on

Table 2

Selected adsorbents-adsorbate pairs with their sorption properties

Adsorbent	Adsorbate	Uptake g/g	Relative pressure p/p_0	Ref
MIL-101(Cr)	H ₂ O	1.60	0.50	[8]
CaCl ₂ -silica	H ₂ O	0.75	0.82	[27]
MIL-125(Ti)-NH ₂	H ₂ O	0.53	0.25	[63]
BUT-46	H ₂ O	0.52	0.40	[65**]
Alfum	H ₂ O	0.35	0.35	[49]
MIL-160	H ₂ O	0.33	0.20	[56]
SAPO-34	H ₂ O	0.31	0.28	[33]
CAU-10-H	H ₂ O	0.30	0.20	[55]
MIL-53(Al)-TDC	H ₂ O	0.28	0.40	[59]
AQSOA®-FAM-Z02H ₂ O		0.27	0.15	[32]
AQSOA®-FAM-Z01H ₂ O		0.18	0.25	[32]
Silica gel	H ₂ O	0.10	0.15	[24]
MIL-101(Cr)	EtOH	0.98	0.30	[2]
KOH6-PR	EtOH	0.90	0.25	[22]
Maxsorb III	EtOH	0.84	0.25	[21]
LiCl-silica	MeOH	0.80	0.32	[28]
Silica gel	MeOH	0.15	–	[28]

the adsorbent–adsorbate working pairs, which are the centerpiece of adsorption chillers or heat pumps. While important MOFs will be discussed in more detail, zeolite, silica gel, activated carbon and some composites with salts will be also mentioned briefly. Some of the selected working pairs are listed in Table 2 with their adsorption properties. Enhancing efficiencies, shaping and a first prototype of a MOF-containing heat exchanger will be mentioned.

Activated carbon

Activated carbons are relatively low-cost hydrophobic materials with typical surface areas up between 300 and 2000 m²/g, even if large surface areas up to 4000 m²/g have been reported [20]. High alcohol and ammonia adsorption capacities make them interesting for AHT application.

Maxsorb III is a commercially available activated carbon with high S(BET) of around 3000 m²/g, and indicated as one of the best candidates for AHT applications using alcohols as adsorbates with an ethanol uptake of 1.2 g/g [18**,21]. Recently, an activated carbon which was obtained from waste palm trunk and mangrove with S (BET) of nearly 3000 m²/g showed an even significantly higher ethanol uptake with 1.8 g/g than Maxsorb III [21].

Another important example is the activated carbon KOH6-PR, which was prepared from phenol resin. KOH6-PR recorded as its highest ethanol adsorption ca. 2 g/g [22].

Silica gel

As mentioned above silica gel is one of the most used adsorbents in commercially available AHTs. Although

silica gel has a quite linear water uptake curve instead of the ideal S-shaped isotherm with an overall low water uptake of 0.03–0.1 g/g for a typical AHT cycle giving a low heat storage capacity [23,24], silica gel is preferred as adsorbent mainly because of its low cost and stability. In contrast, the COP_C value can reach nearly 0.9 due to the lower affinity of silica gel to water vapor, requiring also only a low heat of desorption input [25]. Because of the low cost and availability, the development of AHTs based on silica gel focuses in recent years generally on the design and formation of composite materials. For instance, a recently developed new AHT technique, called ‘Heat from Cold’ (HeCol), uses LiCl-silica gel/methanol as working pairs. In the HeCol technique, depressurization is applied at low ambient temperature for regeneration instead of regeneration at a constant pressure by heating up to 80–150°C, which is the case for conventional regeneration cycles of an adsorption heat pump. This method has the advantages to be applied in colder climates for heat pumping mode [26].

Screening simulation including silica gel, zeolite and activated carbon as adsorbent and water, methanol and ethanol as adsorbate indicate LiBr-silica and CaCl₂-silica (water adsorption of 0.75 g/g at $p/p_0 = 0.82$ and 28°C [27]) as one of the best adsorbents with the working fluid water for air conditioning and heat pumping. COP_H and COP_C value of these composites with water are around 1.62 and 0.71, respectively. Heating and cooling enthalpy of that working pairs are around 1080 kJ/kg (300 Wh/kg) and 570 kJ/kg (158 Wh/kg). The LiCl-silica/methanol working pair (MeOH adsorption of 0.80 g/g at $p/p_0 = 0.32$ and 28°C [28]) exhibited a high performance for air conditioning cycles, with a cooling enthalpy $Q_{ev} = 640$ kJ/kg (178 Wh/kg). For refrigeration, where water cannot be used because of freezing, LiBr-silica with methanol and ethanol was indicated as the best promising working pair with COP_C in the range 0.53–0.59 having a cooling enthalpy of 180 kJ/kg (50 Wh/kg) [29*].

Zeolites

Zeolites are naturally occurring as well as synthetic porous materials based on the combination of [SiO₄] and [AlO₄] tetrahedrons with different ratio of Si to Al. One of the biggest disadvantageous of zeolites for AHT is their too high hydrophilicity, which requires higher desorption temperatures up to 120°C [30].

Ion exchange in the zeolites allows tuning their vapor sorption properties. In a recent example, this was achieved by stirring zeolite with magnesium nitrate solution resulting in up to 42% and 24% more water uptake, at $p/p_0 = 0.2$ and 0.9, respectively [31]. This improvement also held for the sorption performance of the ion exchanged zeolite with an adsorbate mixture of 20% MeOH and 80% H₂O. The MeOH-H₂O mixture has a lower boiling point (86°C) than water alone which means

a heightened vapor pressure and lower freezing point (−18°C). Because of the depressed freezing point, the evaporator can be used at subzero temperatures, below the freezing point of water. This could be beneficial to enhance the cooling efficiency of adsorption heat pumps [31].

In the above simulations, Mitsubishi’s adsorbent AQSOA®-FAM-Z02 (water uptake of 0.27 g/g at $p/p_0 = 0.15$ [32]) and the SAPO-34 zeolite (water uptake of 0.31 g/g at $p/p_0 = 0.15$ [33]) with water as adsorbate was denoted as one of the best working pair candidates for air conditioning and heat pumping similar in performance to LiBr-silica and CaCl₂-silica. The COP_C, COP_H, cooling enthalpy and heating enthalpy of AQSOA®-FAM-Z02 and SAPO-34 were similar to LiBr-silica and CaCl₂-silica (see above) [29*].

The disadvantageous large size (volume) of AHT devices was addressed by using zeolite ferroaluminophosphate (FAM-Z01 with a water uptake of 0.18 g/g at $p/p_0 = 0.25$ [32]) [34]. FAM-Z01 enabled a reduction of system size with comparable COP_C (0.59 for FAM-Z01 and 0.61 for silica gel) and larger specific cooling power (280 for FAM-Z01 and 207 for silica gel) than regular density type silica gel/water (all values at evaporation temperature of 10°C and regeneration temperature of 70°C).

MOFs

Metal-organic frameworks (MOFs) are metal-ligand coordination networks with organic ligands containing potential voids [35]. Porous MOFs are getting continuous attention because of their well-defined network structure, their variability and tunability. Besides possible use for gas storage-separation, catalysis or drug delivery [36], MOFs promise potential for heat transformation applications. Among more than 70 000 different MOFs (until 2017) [37] only a few of them are suitable for heat transformation applications. An essential property which must be fulfilled for AHT is a very high hydrothermal stability which drastically limits the available number of MOFs as many of them are not very water stable [38]. In this minireview, we cover only the promising ones based on uptake capacity and hydrothermal stability.

MIL-101(Cr) is a hydrothermally synthesized MOF with terephthalate (benzene-1,4-dicarboxylate) as linker and a very large surface area up to 4100 m²/g and S-type vapor sorption isotherm above 0.4 relative vapor pressure with water uptakes of up to 1.6 g/g [8]. Over 40 water sorption cycles MIL-101(Cr) showed very little loss (3.2%) on the water sorption capacity [39]. Although the steep part of the sorption isotherm does not take place in the desired relative pressure range, the highest water uptake in the field of MOF chemistry below 0.6 relative pressure make MIL-101(Cr) and its derivatives very attractive for the

many research groups. The focus is to create a more hydrophilic structure preserving the fundamental skeleton of MIL-101. The effect of water sorption by even partial functionalization of the linker benzene ring with hydrophilic $-\text{NHCOCHCHCOOH}$, $-\text{NH}(\text{CH}_2)_3\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{NO}_2$ and $-\text{NH}_2$ groups showed a hydrophilic shift to lower relative pressure. However, owing to the space required by the functional groups a simultaneous reduction of the water sorption capacity relative to the parent MIL-101(Cr) was often observed [13,40].

Grafting of hydrophilic ligands, for example 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane (PAPTS), on coordinatively unsaturated chromium sites is also another approach to tune water uptake of MIL-101(Cr) to relative low vapor pressure [41]. Although water uptake of PAPTS-grafted MIL-101(Cr) at $p/p_0 > 0.4$ is lower compared to the parent MIL-101(Cr), the grafted MIL-101(Cr) adsorbs about 25% more water than native MIL-101(Cr) at a relative pressure of 0.4 [41]. A grafting strategy was also previously applied on the still too hydrophobic MIL-100(Cr), to try to achieve enhancement of water uptake especially in the desired low relative pressure range [42].

The composite of MIL-101(Cr) with 62 wt% CaCl_2 salt loading [43[•]] has only a low remaining S(BET) of $330 \text{ m}^2/\text{g}$, but the water vapor uptake was not too much reduced, due to the absorption capacity of the incorporated hygroscopic salt. Thus, the $\text{CaCl}_2@\text{MIL-101(Cr)}$ composite featured an improved energy storage capacity with a very high value of 450 Wh/kg [43[•]], compared to 87 Wh/kg of parent MIL-101(Cr) in the cycle conditions of 30°C and 1.2 kPa for adsorption and 80°C and 1.25 kPa for desorption [44[•]].

The usage of MIL-101(Cr) as a working pair with alcohols for adsorption chillers is controversial. The high affinity of alcohols to MIL-101(Cr) requires higher desorption temperature related to the Type-I(b) sorption isotherm up to $p/p_0 \approx 0.1$ with an uptake of about 0.46 g/g out of a total uptake of about 1.1 g/g up to $p/p_0 \approx 0.3$ [2]. Yet, this behavior may not necessarily prevent for the usage of MIL-101(Cr) in adsorption chillers and other data indicated a better performance over known activated carbons in terms of uptake of 0.51 g/g of ethanol in the operating conditions 120°C–29°C–7°C (temperature level of heat source, heat rejection/condenser, and evaporator) [45]. Furthermore, in the screening experiments for the working pairs, MIL-101(Cr) and ethanol were designated as one of the best combinations [18^{••}]. Both for EtOH and MeOH, the maximum COP_H value of MIL-101(Cr) was slightly higher than 1.2, which is more than is given in the same work for the activated carbon AX-21/ NH_3 working pair (max. COP_H \approx 1.17) or silica gel salt composite (SP18)/ CaCl_2 (23 wt%) and MeOH (max. COP_H \approx 1.15) [18^{••}]. The cycling operating conditions were 50°C

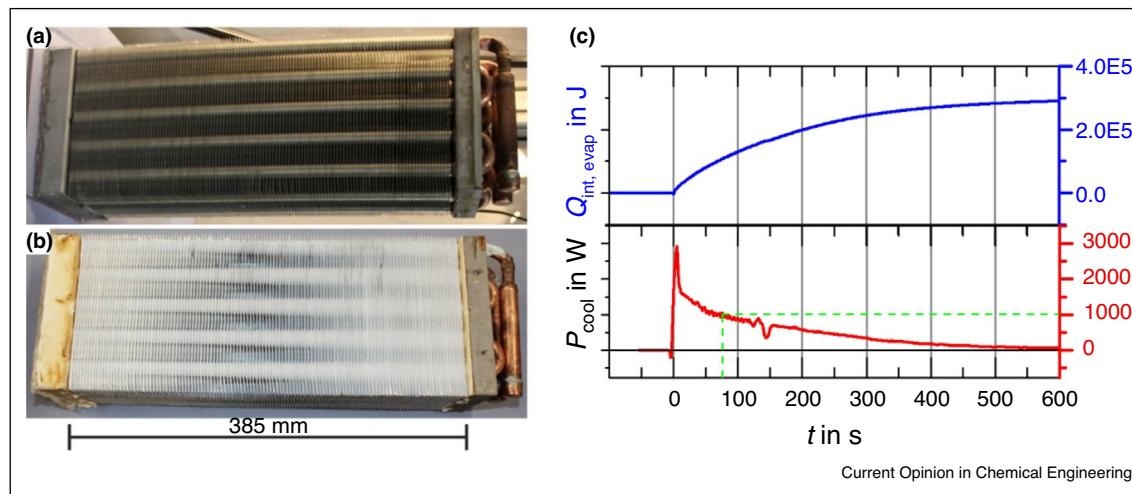
(adsorption and condenser temperature), 5°C (evaporator temperature) for the cooling mode and 50°C (adsorption and condenser temperature), -23°C (evaporator temperature) for the heating mode.

The microcrystalline MOF powders are not susceptible to be used in heat exchangers without formulation, due to dusting because of small particle size and their low thermal conductivity [46]. Shaping of MOFs is, therefore, an important issue for AHT applications. Shaping aspect can be addressed by embedding MOFs in organic polymers, for example, MIL-101(Cr) powder in resorcinol-formaldehyd (R,F) xerogels. This led to formation of stable monolithic forms with a loading of up to 77 wt% of MIL-101(Cr). The composite showed the S-shaped isotherm of the neat MOF and a water uptake of up to 0.88 g/g, which corresponds to 100% retention of pore accessibility of the embedded MOF [47].

Aluminum fumarate (Alfum, commercially also known as BasoliteTM A520) is one of the MOFs, which can be produced from cheap aluminum salts and fumaric acid in water at 60°C [48]. Alfum has a S(BET) of around $1000 \text{ m}^2/\text{g}$ and an S-type water sorption isotherm with an uptake up of nearly 0.35 g/g in the narrow relative pressure range of 0.2–0.3 [49]. Theoretical calculations support the much better cooling performance for Alfum compared to silica gel and AQSOA-Z02, which are currently used in commercially available devices [50]. Alfum showed no degradation over 4500 adsorption-desorption cycles [49]. Because of its high feasibility for AHT applications, a 385 mm × 160 mm × 110 mm heat exchanger was coated with 493 g Alfum, which exhibited a gross cooling power of 2900 W (at the beginning of the adsorption cycle, Figure 2c), 1000 W for a half cycle time of $t = 74$ s or an average cooling power of 690 W (up to a limit of 90% equilibrium loading in 7 min) under the working conditions of a realistic adsorption chiller of 90°C–30°C–18°C (temperature level of heat source, heat rejection/condenser and evaporator) [51[•]]. Related to this matter, cycle duration varies depending on the working point of the devices. For instance, a recommended cycle switch time, being an essential parameter for cooling capacity, should be at least two minutes [52]. A very important figure of merit for an adsorption module is the volume specific heating/cooling power (VSHP/VSCP)

$$\text{VSHP} = \frac{Q_{\text{ads}} + Q_{\text{cond}}}{2\tau_{\text{hc}} V_{\text{mod}}}, \quad \text{VSCP} = \frac{Q_{\text{evap}}}{2\tau_{\text{hc}} V_{\text{mod}}}$$

Wherein τ_{hc} represents the time of a half cycle and V_{mod} the volume of the module. As has been shown in the literature [53] COP and VSHP/VSCP are somehow contradictory. This can clearly be seen from Figure 2c, where the power decreases with time, whereas the amount of heat contributing to the COP increases. Consequently,

Figure 2

Heat-exchanger **(a)** before and **(b)** after coating with 493 g of the aluminum fumarate MOF and drying. **(c)** Gross cooling power P_{cool} of the aluminum fumarate-coated heat exchanger for operating conditions 90°C–30°C–18°C (red line, lower part; temperature level of heat source, heat rejection/condenser and evaporator), calculated from the integral heat of evaporation $Q_{\text{int},\text{evap}}$ (blue line, upper part). The green line indicates $P_{\text{Cool}} = 1000 \text{ W}$ for a half cycle time of $t = 74 \text{ s}$.

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the cycle time is an optimization parameter that can be chosen with respect to either a higher COP or a higher VSHP/VSCP.

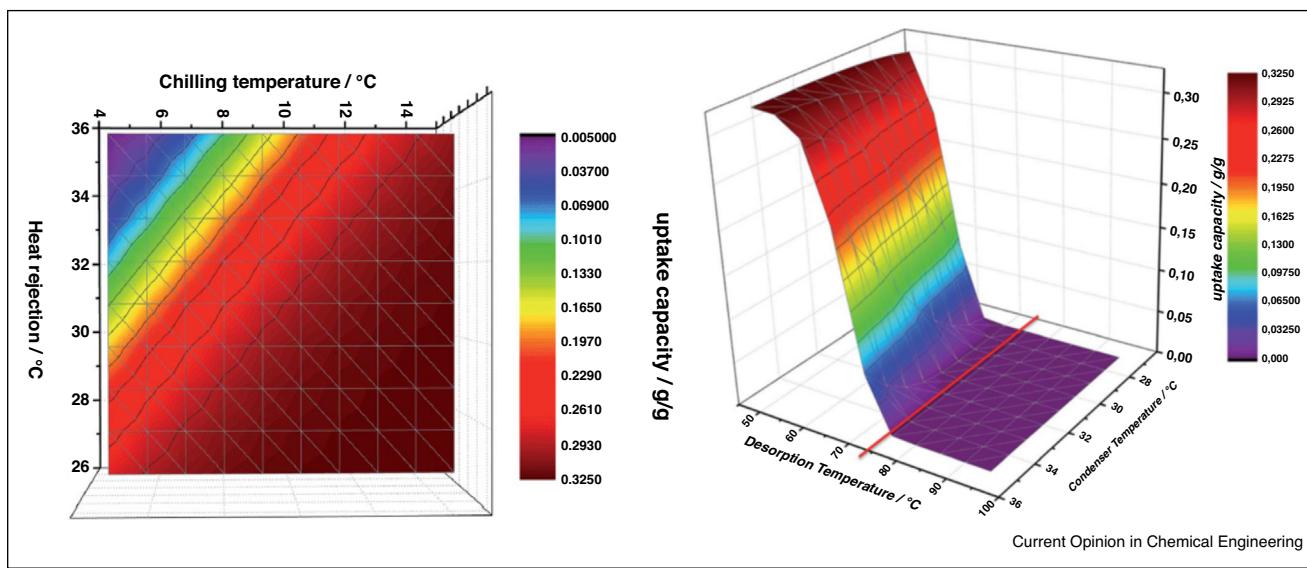
Furthermore, adding excess formic acid as a modulator to the preparation of aluminum fumarate showed that water adsorption kinetics can be improved due to the enhanced uniform micro-pore distribution [54]. Starting from the adsorbed state at $p/p_0 = 0.3$, 25°C, for instance, Alfum formed by addition of formic acid achieved the thermodynamic desorbed equilibrium state at $p/p_0 = 0.25$, 60°C in 1600 s, whereas Alfum without any additional formic acid achieved the same equilibrium in 3000 s. In that work, the modulator was applied in a problematic dimethylformamide (DMF) based synthesis, which should be modified to a water-based preparation in the interest of green chemistry.

CAU-10-H is another promising MOF for water sorption-based applications [55]. This MOF consists of aluminum metal ions, hydroxido bridges and isophthalate linkers. It possesses an S-shaped water sorption with an uptake around 0.30 g/g at a relative vapor pressure of about 0.2 [55]. The cyclic stability of CAU-10-H was tested up to 10 000 water adsorption–desorption cycles showing no loss in water loading and crystallinity. At present, CAU-10-H was denoted as the most hydrothermal stable MOF under cycling conditions between 40°C adsorption and 140°C desorption temperature [12]. Figure 3 left presents the water uptake capacity of CAU-10-H at different heat rejection and chilling (evaporating) temperature during the adsorption process (working cycle in

Figure 1). The maximum water uptake (dark red region) can be reached at a chilling temperature above 12°C together with a maximum heat rejection temperature of about 32°C. Alternatively, if the heat rejection is lowered to 26°C, the chilling temperature can drop to about 6°C. Additionally, for regeneration (regeneration cycle in Figure 1) the desorption temperature is most important and can be as low as 75°C (red line in Figure 3 right) in order to achieve complete drying of the adsorbent. At the same time, the condenser temperature can vary from 28 to 35°C [12].

MIL-160 is based on Al^{3+} with the linker 2,5-furandicarboxylate [44*], isostructural to CAU-10-H, and shows promising water sorption properties with an uptake of around 0.33 g/g at $p/p_0 \approx 0.2$ [56]. Albeit not emphasized, part of the aforementioned studies with Alfum and CAU-10-H was also the shaping of the MOFs with polysiloxane binders to achieve a stable coating on the metal support (cf. Figure 2) MIL-160 was shaped into pellets via wet granulation and exhibited similar, mass-corrected sorption properties as the neat MOF. A heat-reallocation open-system reactor prototype containing MIL-160 pellets revealed one of the best performances with an energy storage density of 141 kW h/m³, which is slightly higher than the energy storage density of Zeolite 13 X with a value 131 kW h/m³, both after complete evacuation [44*].

MIL-53(Al)-TDC with Al^{3+} and the linker 2,5-thiopnedicarboxylate [57] was first predicted to show good water sorption properties [58]. In the follow-up experimental study, MIL-53(Al)-TDC was shown to have a

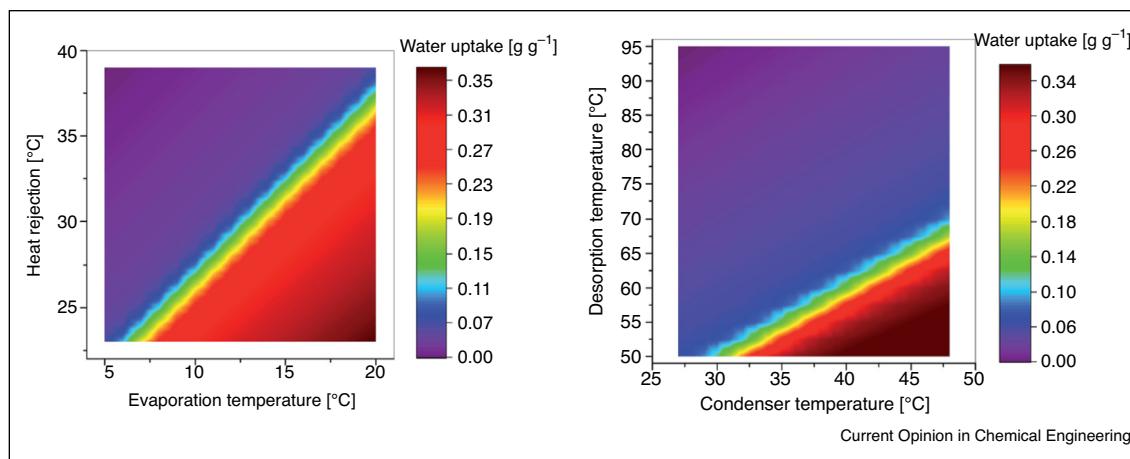
Figure 3

Left: water uptake capacity of CAU-10-H as a function of heat rejection temperature and evaporation (chilling) temperature. Right: Desorption temperature and condenser temperature necessary to achieve adsorbent regeneration (drying, water removal). (Note that in the original publication, the respective figure captions or figures need to be interchanged).

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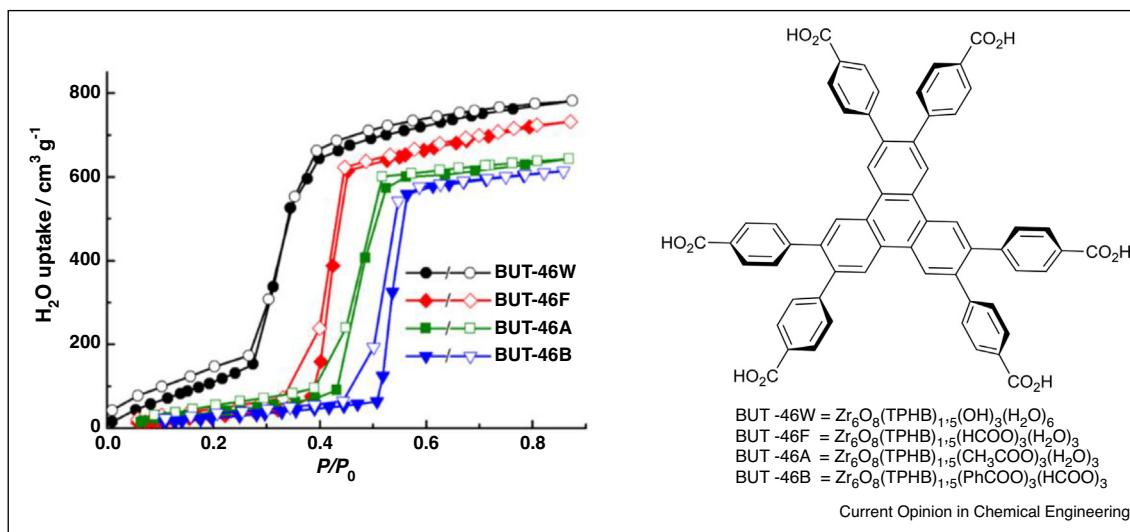
higher surface area and suitable water sorption properties than was estimated before. The hydrothermal stability of MIL-53(Al)-TDC was tested to over 40 adsorption-desorption cycles with feasible water uptake of 0.28 g/g at around $p/p_0 = 0.4$ without little hysteresis and the low heat of adsorption ($2.6 \text{ kJ/g} = 0.72 \text{ Wh/g}$). These properties make MIL-53(Al)-TDC a good candidate for adsorption-based chillers [59]. In Figure 4 left, it can be seen

that the maximum water uptake (dark red region) can be reached at an evaporation temperature above 15°C together with a heat rejection temperature below 25°C. Additionally, for regeneration (regeneration cycle in Figure 1) the desorption temperature can be as low as 55–60°C (Figure 4 right), with the condenser temperature above 40°C in order to achieve complete drying of the adsorbent.

Figure 4

Left: water uptake capacity of MIL-53(Al)-TDC as a function of heat rejection temperature and evaporation temperature. Right: Estimation of water uptake capacity as a function of desorption temperature and condensing temperature.

Figures were taken from Ref. [59] with permission from the author, copyright the Royal Society of Chemistry 2018.

Figure 5

Left: water adsorption–desorption isotherms of the BUT-46 series. Right: Chemical structure of H_6TPHB ligand and molecular formulae of the BUT-46 series.

Figure 5 left was used with permission from Ref. [65**], copyright the American Chemical Society 2018.

MIL-53(Al)-TDC gave below 0.1 p/p_0 a steep uptake of ethanol, however with a very strong (unclosed) hysteresis in the desorption curve [60].

Another important candidate for AHT application is **MIL-125(Ti)-NH₂** [61]. As it showed promising water uptake of slightly over 0.30 g/g at 20°C with an S-shaped isotherm in the relative pressure range of 0.1 and 0.25 [62]. Over 40 adsorption–desorption cycles MIL-125(Ti)-NH₂ exhibited a degradation of 17%. Later on, the synthesis using Ti(BuO)₄ instead of Ti(iPrO)₄ as Ti sources led to improved 0.50 g/g water uptake even at 35°C in the relative pressure range of 0.1 and 0.25 [63,64]. Over 10 adsorption–desorption cycles the new MIL-125(Ti)-NH₂ showed only very low decrease in water uptake. Yet, to consider this MOF further for AHT devices it must be clearly be tested for more adsorption–desorption cycles.

An isostructural **BUT-46** series, with Zr⁴⁺ as metal ion, TPHB⁶⁻ (4',4'',4''',4''''-(triphenylene-2,3,6,7,10,11-hexyl)hexabenoate) as linker and different terminal functional groups show promising water sorption properties at the relative pressure of 0.4 with a steep uptake of around 0.52 g/g [65**]. Although the members of the BUT-46 series have similar S(BET), changing the terminal functional groups affects hydrophilicity (p/p_0 range) and water uptake capacity of the MOFs (Figure 5). However, the multistep synthesis of the linker may make these MOFs unattractive for larger-scale applications.

Conclusion

AHT applications are receiving a strongly renewed interest in the last decades because they are economical and ecologically beneficial compared to conventional heat transformation, for example, electricity-run compressor air conditioners. However, the existing adsorbent materials such as silica gel used in the commercial available devices suffer from their low efficiency. MOFs were for about 10 years now investigated more specifically for cycling water sorption for heat transformation and gave the opportunity to enhance and tune vapor sorption through their designable pore structures. In the last years MOFs were developed with promising water sorption properties such as the desired S-shape isotherm in a low p/p_0 region, high water uptake and hydrothermal stability. However, one of the disadvantages of the MOFs is the more expensive production cost, the necessity for shaping the otherwise microcrystalline powders and the still not fully long-term proven stability. Considering the easy synthesis of MIL-160, which is prepared under reflux from aluminum salts and 2,5-furandicarboxylate (which can be derived from renewable biomass), MIL-160 could be an alternative to SAPO-34. Additionally, Alfum is easy to prepare from abundant starting materials and could be an alternative for silica for cooling purposes. On the other hand, composite materials of zeolites and silica gel with salts like LiCl or CaCl₂ are also gaining interest for their increased uptake and heat transformation enthalpies.

Conflict of interest statement

Nothing declared.

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In this publication, tunability of the MOF structure was shown by functionalization of the linker. Thereby S-shapes of water sorption isotherms were achieved in different relative pressure ranges.