Experimental Study on Heat Transfer and Adsorption Cooling Performance of MIL-101/Few Layer Graphene Composite

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Abstract: MIL-101 is a promising metal-organic frameworks (MOFs) material in adsorption chiller application due to its high adsorption capacity for water and excellent adsorption/desorption cyclic stability. Few layer graphene (FLG) as the thermal conductive additive was added into MIL-101 to improve inferior heat transfer of MIL-101 in the adsorption cooling process. The heat transfer characteristic of MIL-101/FLG adsorber and the adsorption cooling performance of the MIL-101/FLG-water working pair were studied. Results show that thermal conductivity of MIL-101/20%FLG composite is 5.79-6.54 times that of MIL-101. Adding FLG is conducive to the formation of heat transfer channels in MIL-101/FLG adsorber and the rapid removal of adsorption heat. The heating and cooling rate of MIL-101/FLG adsorber is ~2.2 times that of MIL-101 adsorber. Under typical adsorption water chiller conditions, the specific cooling power (SCP) and coefficient of performance (COP) of the MIL-101/FLG-water working pair is 72.2–81.0 W kg\(^{-1}\) and 0.187–0.202, respectively, at desorption temperatures of 70 °C and 90 °C, which is 1.43–1.56 times higher than the MIL-101-water working pair. The excellent structural and adsorption/desorption cyclic stability of MIL-101/FLG composite is verified after 50 consecutive cycles. It can provide a promising adsorbent candidate (MIL-101/FLG composite) in adsorption water chiller process.

Keywords: adsorption cooling; heat transfer characteristic; MIL-101; few layer graphene; specific cooling power; water chiller

1. Introduction

Adsorption cooling technology [1,2] can be utilized to obtain cooling capacity through the adsorption process of environmentally-friendly refrigerants on solid adsorbents, which is a promising cooling mode with fine operation stability and low cost [3,4]. This cooling technology can be driven by low-grade heat energy; hence, the consumption of high-grade electrical energy can be effectively reduced [5,6]. For the reasons of high latent heat of vaporization [7] (–2400 kJ kg\(^{-1}\)) as well as non-toxic and environmental protection [8], water is the most commonly used refrigerant, and the water-based adsorption cooling working pairs mainly include silica gel [9–14], zeolites (SAPO-34 [15], ZSM-5 [16], AQS0A [17], FAM Z01 [18], 13X [19] and metal-organic frameworks (MOFs, such as MIL-100 [20], MIL-101 [21,22], ISE-1 [23] and MOF-801 [24]). Some adsorbent-refrigerant working pairs like silica gel-water [12], siliceous shale impregnated LiCl-water [25] and AQS0A FAM-Z02-water [26] have been utilized in adsorption chiller application. Currently, some possible application directions of adsorption water chiller (16–20 °C) include proton exchange membrane fuel cell [27], automotive engine coolant [28], vehicle air-conditioning [29] and data center cooling [30,31]. The heat generated in fuel cell stacks (temperatures of 70–95 °C), internal combustion engines (100–130 °C) and server chipsets (temperatures of 70–90 °C) all could be used to drive the adsorption chiller. Although the
desorption temperature of silica gel was low (65–100 °C), the cyclic adsorption capacity of water on silica gel was only 0.03–0.30 g kg\(^{-1}\) \(1_{ads}\) [11]. The desorption temperature of water on the molecular sieve exceeded 200 °C [19]. MIL-101 (Cr) is considered as one of the most promising MOF materials in the field of adsorption chiller due to its high BET specific surface area (3000–4000 m\(^2\)/g), large adsorption capacity (1.40–1.50 g kg\(^{-1}\) \(1_{ads}\)) for water [32], excellent adsorption/desorption cyclic stability [33] and good high-temperature thermal stability [34] (<400 °C). Wang et al. [35] reported that a steep adsorption uptake of water rises on MIL-101 (Cr) under P/P\(_0\) of 0.35–0.55 (evaporation temperature of 16–18 °C) along with superior hydrothermal stability, which is a promising application for data center cooling or vehicle air-conditioning, etc. Moreover, the desorption capacity of water on MIL-101 (Cr) is ~70% at 70 °C (~0.90 g kg\(^{-1}\) \(1_{ads}\)) and almost completely desorbs at 110 °C (~1.40 g kg\(^{-1}\) \(1_{ads}\)). The experimental cooling performance of MIL-101 (Cr)-water [36] and MIL-101 (Cr)-ethanol working pair [37] has been effectively evaluated by our group on an adsorption cooling device system. However, the poor thermal conductivity of MIL-101 (Cr) powder [38] (~0.06 W m\(^{-1}\) K\(^{-1}\)) results in a slow removal rate of adsorption heat, long heating and cooling time in the adsorption cooling process. Therefore, it is vital to strengthen the heat conduction property of MIL-101 (Cr) by the addition of FLG to improve adsorption cooling performance of MIL-101 (Cr)-water working pair.

The heat transfer performance of adsorbers and cooling performance (SCP/COP) of adsorption cooling working pairs could be effectively improved by adding thermal conduction materials to strengthen the thermal conductivity of the solid adsorbents. Chen et al. [39] indicated that a heat transfer temperature difference of a 13X molecular sieve/iron adsorption bed decreased by 30%. The cooling capacity of a 13X molecular sieve/iron filling-water adsorption cooling system was 1.19 W and 23.7% that of a 13X-water adsorption cooling system under the same working conditions. 13X molecular sieve/aluminum foam composite was prepared by Hu et al. [40] with a volume fraction of 15–20 vol% aluminum foam, and there was no obvious heat transfer temperature difference inside the 13X/aluminum foam adsorber. The SCP of a13X molecular sieve/aluminum foam-water adsorption cooling system was ~450 W kg\(^{-1}\) and increased by ~2 times that of 13X molecular sieve-water. A silica gel/aluminum foam composite adsorber was constituted by Mohammed et al. [41]. The result of simulative calculation showed that the SCP and COP of a silica gel/aluminum foam-water working pair were 577 W kg\(^{-1}\) and 0.79, respectively, which was 1.3 times and 11.3% higher than that of the silica gel-water working pair at an evaporation temperature of 10 °C, desorption temperature of 85 °C and condensation temperature of 30 °C. 13X molecular sieve-CaCl\(_2\)/MWCNT (multi-walled carbon nanotubes) composite was prepared by Chan et al. [42]. The thermal conductivity of 13X molecular sieve-CaCl\(_2\)/MWCNT (mass fraction of 1 wt%) was 0.2719–0.3767 W m\(^{-1}\) K\(^{-1}\). The SCP and COP of a 13X molecular sieve-CaCl\(_2\)/MWCNT-water working pair were 1113.4 W kg\(^{-1}\) and 0.26 by simulative calculation at a desorption temperature of 80 °C and adsorption temperature of 30 °C. The thermal conductivity of compressed silica gel/expanded graphite (EG) composites was found to be higher than 10 W m\(^{-1}\) K\(^{-1}\) with the addition of 20–40 wt% EG (volume density >0.2 g cm\(^{-3}\)) by Eun et al. [43,44]. SCP of silica gel/30wt%EG-water adsorption cooling system was 37 W kg\(^{-1}\) and improved by 76% at an adsorption temperature of 25 °C, evaporation temperature of 8 °C, desorption temperature of 80 °C and condensation temperature of 30 °C. A 13X molecular sieve/12wt%EG composite was prepared by Wu et al. [45] and its thermal conductivity was 0.2536 W m\(^{-1}\) K\(^{-1}\). The cycle time of water on a 13X molecular sieve/EG composite was 203 min and was 11.4% shorter than that of 13X molecular sieve. Compared to 13X molecular sieve–water working pair, the SCP (46.12 W kg\(^{-1}\)) and COP (0.328) of a 13X molecular sieve/12wt%EG–water working pair improved by 24% and 10.4%, respectively, at a desorption temperature of 300 °C. A silica gel-CaCl\(_2\)/graphite composite was prepared by Bahrehmand et al. [46,47]. The thermal diffusivity of silica gel-CaCl\(_2\)/20wt%graphite composite was 0.375–1.38 mm\(^2\) S\(^{-1}\). The cooling rate of silica gel-CaCl\(_2\)/20wt%graphite composite was 0.115 °C min\(^{-1}\) and 1.5 times as much as that of silica gel-CaCl\(_2\).
In summary, the heat transfer property of silica gel and a 13X molecular sieve as well as the adsorption cooling performance of these composite materials/water working pairs could be enhanced by adding thermal conductive materials (metal, metal foam, multi-walled carbon nanotubes, graphite, etc.), which has been reported. Graphene is also a promising thermal conductive carbon material [48–50]. The thermal conductivity of graphene [51,52] and FLG [53,54] can reach as high as 2000–5000 W m\(^{-1}\) K\(^{-1}\) and 500–2000 W m\(^{-1}\) K\(^{-1}\), respectively. Most of the literature on the adsorption cooling performance of MOFs has been based on simulative calculations of adsorption isotherm and adsorption kinetics, and there are few relevant reports on experimental studies. So far, adding few layer graphene (FLG) into MIL-101 (Cr) (herein MIL-101) for the enhancement of the heat transfer characteristics of an MIL-101/FLG adsorber and the adsorption cooling performance of an MIL-101/FLG composite-water working pair have not been reported. Moreover, there is also no report on an experimental adsorption cooling process of MOF composite-water working pairs in an adsorption water chiller application.

In this paper, FLG was added into MIL-101 for the enhancement of thermal conduction. The thermal conduction property of MIL-101/FLG composite adsorbents was determined. Heat transfer characteristics of MIL-101/FLG adsorbers during the adsorption cooling process were investigated. The heat transfer mechanism of MIL-101/FLG was analyzed. The adsorption cooling performance of MIL-101/FLG-water working pairs was investigated and compared to MIL-101-water working pairs under specific working conditions of the adsorption water chiller process. Moreover, the adsorption cooling cyclic stability of MIL-101/FLG-water working pairs was determined. The heat transfer characteristics and adsorption cooling performance of MIL-101/FLG-water working pairs were improved by incorporation of thermal conductive FLG, which could be conducive to increasing the energy conversion efficiency in adsorption water chiller applications. The results of this paper provide basic research for the utilization of an MIL-101/FLG composite in adsorption water chiller processes.

2. Materials and Methods

2.1. Preparation of MIL-101/FLG Composites

MIL-101 was prepared by a hydrothermal method [37,55], while the preparation method of MIL-101/FLG composites was described in our previous work [56].

2.2. Characterization Methods of MIL-101/FLG Composites

The surface micro morphology of FLG was conducted by scanning electron microscopy (SEM, Japan Hitachi, S4800). The crystal defects of FLG were measured by Raman spectra (Japan Horiba, Labram HR800, shift of 1000–3000 cm\(^{-1}\)). The crystal structures of FLG, MIL-101/20%FLG before and after the adsorption cooling cycles were analyzed by X-ray diffraction (XRD, Japan Rikagu, SmartLab) with the diffraction angles ranging from 2–30°. \(\text{N}_2\) adsorption/desorption isotherms of MIL-101/20%FLG before and after the adsorption cooling cycles at 77 K were measured on the BELSORP-max (Japan microtrac bayer) adsorption analyzer. The surface area was calculated by BET equation and the pore volume was calculated by t-plot methods.

2.3. Measurement of Thermophysical Properties of MIL-101/FLG Composites

As shown in Figure 1a,b, the powdered MIL-101/FLG and MIL-101 samples were shaped into cylindrical specimens (density of 0.55 g cm\(^{-3}\)) under a pressure of 3.0–4.0 MPa and subsequently activated at 120 °C for 2 h.
Thermophysical properties of MIL-101 and MIL-101/FLG composite were measured at 30–130 °C on a TPS-2500S type thermal property instrument (Hot-Disk Co., Ltd., Uppsala, Sweden). The thermal conductivity and specific heat capacity were measured through the “ISO22007-2-2015” standard [57,58]. The theoretical calculation equations of thermophysical properties refer to our previous work [56]. The standard deviations (error bars) of experimental results are shown in the results and discussion.

2.4. Determination of Adsorption and Desorption Performance of MIL-101/FLG Composite

The measuring methods of adsorption isotherms of water on MIL-101 and MIL-101/FLG composites and thermogravimetric-differential analysis (TG-DTA) curves of water on MIL-101 and MIL-101/FLG composites were described in our previous work [56]. The adsorption isotherms of water on MIL-101/FLG and MIL-101 were determined at 25 °C on a BELSORP-max (volumetric method) adsorption analyzer, while the adsorption rate curves of water on MIL-101/FLG and MIL-101 were measured at 25 °C by a high vacuum adsorption instrument (gravimetric method) and the adsorption pressure was 2500–2600 Pa.

2.5. Determination Method of Adsorption Cooling Performance of MIL-101/FLG-Water Working Pairs

The heat transfer characteristic of MIL-101/20%FLG adsorbers and adsorption cooling performance of MIL-101/20%FLG-water working pairs were investigated on a cyclic adsorption cooling device (shown in Figure 2).
The main components in an adsorption cooling device are the adsorber, condenser, evaporator, refrigerator, heating furnace, vacuum pump and level gauge (0~220 mm, accuracy of 0.1 mm). The central and outer wall temperatures of the adsorber were measured by a Pt-100 type resistance (−30~200 °C, accuracy of ±0.1 °C). The center and outer wall temperatures of the adsorber were real-time recorded by a WP-MD807-71-23-HL type (accuracy of ±0.1 °C) intelligent multiway inspection display controller. The adsorber-heat exchanger was a glass cylinder (inner diameter of 32 mm and height of 400 mm) and total mass of 314.2 g. As seen in Figure 1c,d, the MIL-101/FLG and MIL-101 particles (particle size of about 380–830 μm) for loading into the adsorber were obtained by crushing and sieving the cylindrical specimens formed by the tablet press. The loading mass of MIL-101/FLG and MIL-101 in the adsorber was 25.0 g and 24.5 g, respectively; meanwhile, the loading volume of MIL-101/FLG and MIL-101 adsorption beds was 0.156 L and 0.142 L, respectively. Adsorption cooling performance was directly investigated on the MIL-101/FLG composite or MIL-101 fixed-bed under the same system configuration. Refer to the literature for the detailed experimental procedures [59].

The calculation equations of cooling capacity ($Q_c$), SCP and COP [60] are shown in Equations (1)–(5).

$$Q_c = \frac{\Delta mad \cdot \Delta H_e}{\Delta t}$$

(1)

$$Q_{evap} = \Delta mad \cdot \Delta H_e$$

(2)

where $Q_c$ is the cooling capacity per unit of cycle time, W; $\Delta mad$ is the amount of cycled water, kg; $\Delta H_e$ is the vaporization latent heat of water at the evaporation temperature, kJ kg$^{-1}$; $\Delta t$ is the cycle time, s; $Q_{evap}$ is the evaporative cooling capacity, kJ.

$$Q_{input} = C_a m_a T_2 - T_1 + C_{lc} m_{lc} T_2 - T_1 + C_m m_m T_2 - T_1 + m_{lc} h_d$$

(3)

where $Q_{input}$ is the heat absorbed during desorption process, kJ; $C_a$, $C_{lc}$ and $C_m$ are the average specific heat capacity of the adsorbent, water and adsorber-heat exchanger, re-

Figure 2. Schematic diagram (a) and overall view (b) of adsorption cooling device system for an MIL-101/20%FLG-water working pair. 1-vacuum pump, 2,3,8-valve, 4-thermostat, 5-condenser, 6-level gauge, 7,9,13-thermocouple, 10-refrigerator, 11-evaporator, 12-vacuum gauge, 14-adsorber, 15-heat exchanger.
respectively. $J$ kg$^{-1}$°C$^{-1}$; $m_{lc}$ and $m_m$ are the mass of desorption of water and adsorber-heat exchanger, respectively, kg; $h_d$ is the desorption enthalpy of water, kJ kg$^{-1}$; $T_1$ and $T_2$ are the initial and final temperatures of the adsorber during the heating desorption process, respectively, °C.

$$SCP = \frac{Q_c}{m_a}$$  

$$COP = \frac{Q_{evap}}{Q_{input}}$$  

where $SCP$ is the specific cooling power of the system per unit mass of adsorbent, W kg$^{-1}$; $m_a$ is the adsorbent mass, kg; $COP$ is the coefficient of performance of the system.

The standard deviations (error bars) of repeat experimental results are shown in the results and discussion. The main uncertainties of $Q_c$, $SCP$ and $COP$ are mainly from the level gauge (Figure 2). The relative error of results was calculated by Equation (6) [47].

$$\frac{\Delta y}{y} = \left[ \sum_{i=1}^{k} \left( \frac{\partial y}{\partial v_i} \right)^2 (\Delta v_i/y)^2 \right]^{1/2}$$  

Herein, the relative error is 1.1% for $Q_c$, $SCP$ and $COP$.

3. Results and Discussion

3.1. Thermal Conductivity of MIL-101/FLG Composites

Thermal conductivities of MIL-101/FLG composites with FLG mass fraction of 5–20% were investigated between 30 °C and 130 °C and the results are shown in Figure 3.

![Figure 3](image-url)

Figure 3. Thermal conductivities of MIL-101/FLG composites and MIL-101 at different measurement temperatures.

Seen from Figure 3, the thermal conductivity of MIL-101 is 0.1272–0.1486 W m$^{-1}$ K$^{-1}$ at 30–130 °C. The thermal conductivity of MIL-101/20%FLG is 0.8322–0.8603 W m$^{-1}$ K$^{-1}$ at 30–130 °C, which is 5.79–6.54 times that of MIL-101, respectively. The thermal conductivity of the MIL-101/FLG composite is below 0.5 W m$^{-1}$ K$^{-1}$ at a low adding amount of FLG (<10%) owing to a poor heat conduction channel. When the content of FLG in MIL-101/FLG composites reaches 20% and is evenly dispersed in MIL-101, the effective thermal conductive pathways can be formed in the MIL-101/FLG composite. Hence, the heat could be quickly transferred through the thermal conductive pathways composed of FLG with minimum thermal resistance, leading to a sudden change of thermal conductivity. The suitable content of FLG added in the MIL-101/FLG composite is 20%.
3.2. Adsorption and Desorption Performance of MIL-101/FLG Composite

The adsorption isotherms and adsorption rate curve of water on MIL-101/20%FLG composites were measured and shown in Figures S1 and S2, while the TG-DTA curves of MIL-101/20%FLG composites were measured and displayed in Figure S3.

As shown in Figure S1, the MIL-101/20%FLG composite could be suitable in adsorption cooling/chiller applications with an evaporation temperature above 15 °C due to the steep uptake of water at P/Ps of 0.40–0.50. Based on the TG-DTA curves of water on MIL-101/20%FLG (Figure S3), the desorption temperature of the MIL-101/20%FLG–water working pair was selected as 70–130 °C according to specific application conditions.

3.3. Temperature Characteristic Curves of MIL-101/FLG Adsorber in Adsorption Cooling Process

The heat transfer characteristic of the MIL-101/FLG adsorber was evaluated by the temperature characteristic curves of MIL-101/20%FLG adsorbers during the adsorption, desorption and cooling process on the adsorption cooling device (Figure 2).

3.3.1. Temperature Characteristic Curves during Adsorption Process

The temperature characteristic curves of MIL-101 and MIL-101/20%FLG adsorbers during the adsorption process were measured at an ambient temperature of 25–30 °C, adsorption temperature of 25–30 °C, evaporation temperature of 17 °C and adsorption time of 120 min, with the results shown in Figure 4.

As shown in Figure 4, within the initial stage of adsorption process (adsorption time of 9 min), the temperature of MIL-101 adsorbers rises from 29.0 °C to 41.7 °C (maximum temperature rise of 12.7 °C), while the temperature of MIL-101/20%FLG adsorbers rises from 29.1 °C to 32.6 °C and the maximum temperature rise is merely 3.5 °C, which is significantly lower than MIL-101 adsorbers. Since the equilibrium adsorption capacity of MIL-101 for water (1.14 g g\textsuperscript{-1} ads) is higher than MIL-101/20%FLG (0.90 g g\textsuperscript{-1} ads), a larger amount of adsorption heat is released by the adsorption process of water on MIL-101 and a higher temperature rise is caused, but the maximum temperature rise for MIL-101/20%FLG adsorbers per unit mass of MIL-101 is just 0.179 °C g\textsuperscript{-1} and still far lower than that of MIL-101 adsorbers (0.508 °C g\textsuperscript{-1}). Hence, the lower maximum temperature rise of MIL-101/20%FLG adsorbers is the combination of adsorption capacity (low heat release rate) and better heat conduction property of MIL-101/20%FLG, so the generated adsorption heat could quickly be transferred to the external environment. As the adsorption process goes on, the adsorption rate decreases while the adsorption heat reduces; it takes 30 min

![Figure 4. Temperature characteristic curves of MIL-101/20%FLG and MIL-101 adsorbers during the adsorption process.](image-url)
(adsorption time of 6–36 min) for MIL-101/20%FLG adsorbers to drop from 32.6 °C to 28.0 °C with a cooling rate of 0.153 °C min\(^{-1}\), while the temperature of MIL-101 adsorbers just falls from 32.6 °C to 29.9 °C in the same duration (adsorption time of 40–70 min) and the cooling rate is merely 0.09 °C min\(^{-1}\). At the low temperature region, the cooling rate of MIL-101/20%FLG adsorbers is 1.7 times that of MIL-101 adsorbers. The thermal conductivity of MIL-101 adsorbers increases, and the rapid removal of adsorption heat is promoted by adding FLG; hence, the temperature rise of MIL-101/20%FLG adsorbers can be reduced during the adsorption process as the cooling rate is accelerated.

3.3.3. Heating Curves in the Desorption Process

The temperature characteristic curves of MIL-101 and MIL-101/20%FLG adsorbers during the heating desorption process were compared at an ambient temperature of 25–30 °C, while the initial temperature of MIL-101 and MIL-101/20%FLG adsorbers was 28.7 °C and 29.0 °C, and the desorption temperature was 130 °C with a desorption time of 40 min. The results are shown in Figure 5.

![Figure 5. Variation of temperatures between outer wall and inner MIL-101/20%FLG and MIL-101 adsorbers during the heating desorption process.](image)

As seen from Figure 5, when the final central temperatures in MIL-101/20%FLG and MIL-101 adsorbers are both ~130 °C, the outer wall temperature of MIL-101/20%FLG and MIL-101 adsorbers is stable around 135 °C and 151 °C, respectively. The heating time of MIL-101/20%FLG adsorbers from 29.0 °C to 130.5 °C is 8 min with a heating rate of 12.69 °C min\(^{-1}\), which is 2.24 times as much as that of MIL-101 adsorbers (heating rate of 5.67 °C min\(^{-1}\), heating time from 28.7 °C to 130.8 °C is ~18 min), and the heating time is shortened by 55.5%. The heat transfer temperature difference between the central and outer wall of MIL-101 adsorbers is about 21 °C, while between the central and outer wall of MIL-101/20%FLG adsorbers, it is only 5 °C and is significantly decreased by 76.2%. This is due to the fact that a thermal conductive channel can be formed within the MIL-101/FLG composite by adding FLG into MIL-101, which improves thermal conduction performance of MIL-101 adsorbers, and the thermal contact resistance between MIL-101 particles is reduced. Therefore, the heat transfer of MIL-101 adsorbers could be effectively improved by adding FLG during the heating desorption process, which would be beneficial to reduce desorption time.

3.3.3. Cooling Rate

At an initial temperature of ~130 °C and final temperature of ~29 °C, the temperature drop curves of MIL-101 and MIL-101/20%FLG adsorbers were measured in the cooling process. The results are shown in Figure 6.
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As seen in Figure 6, the cooling time of an MIL-101/20%FLG adsorber consists of only 27 min to drop from 130.6 °C to 29.0 °C with a cooling rate of 3.76 °C min\(^{-1}\), while an MIL-101 adsorber needs 60 min to drop from 130.4 °C to 29.2 °C with a cooling rate of 1.69 °C min\(^{-1}\). The cooling rate of an MIL-101/20%FLG adsorber is 2.22 times that of an MIL-101 adsorber; hence, the cooling time is shortened by 55%. In the continuous adsorption cooling cycle, compared to an MIL-101 adsorber, the MIL-101/20%FLG adsorber needs a shorter time to switch to the next cycle, which is conducive to improving the SCP of an adsorption cooling system.

3.3.4. Heat Transfer Mechanism

The phase structure, SEM image and Raman spectra of FLG were determined and shown in Figure S4. The results indicate that FLG is a layered structure without surface defects. In combination with the XRD, SEM and Raman characterization of FLG (Figure S4), a schematic diagram of the structure and heat transfer mechanism for an MIL-101/FLG composite were analyzed in Figure 7.

It can be seen in Figure 7a that heat in FLG is both conducted by phonon (lattice vibration wave) heat conduction and electronic heat conduction. As seen in Figure 7b, MIL-101 is a three-dimensional framework mesoporous material, and heat conduction in MIL-101 is mainly achieved by phonon diffusion. Due to its high porosity, severe phonon scattering occurs when heat is transferred in the MIL-101 skeleton, and there is large contact thermal resistance between MIL-101 particles, leading to a low thermal conductivity of only 0.1272–0.1486 W m\(^{-1}\) K\(^{-1}\). As a consequence, the heating and cooling rate of the MIL-101 adsorber was affected. As shown in Figure 7c, since interfacial mutual interactions between FLG and MIL-101 can be promoted after a ball-milling process, a \(\pi-\pi\) stacking effect may be formed between the benzene ring of MIL-101 framework and hex-atomic ring in the layered FLG; namely, certain interactions exist between FLG and MIL-101. Moreover, fast migration of free electrons can be promoted due to the two-dimensional plane structure of FLG (with large surface area). Therefore, thermal resistance between MIL-101 particles is reduced and the thermal conduction of MIL-101/20%FLG composite is effectively improved. As a result, the heating and cooling rate of MIL-101/20%FLG adsorber increases while heating and cooling time is correspondingly shortened.

![Figure 6. Temperature characteristic curves of MIL-101/20%FLG and MIL-101 adsorbers during the cooling process.](image-url)
Figure 7. Schematic diagram of structure and heat conduction mechanism for (a) FLG, (b) MIL-101 and (c) MIL-101/FLG composite.

3.4. Adsorption Cooling Performance of MIL-101/20%FLG-Water Working Pair

The effects of working condition parameters on the adsorption cooling performances (cooling capacity and cooling power) of an MIL-101/20%FLG-water working pair were investigated on the adsorption cooling device (Figure 2). The working condition parameters of the MIL-101-water working pair are shown in Figures S5 and S6.

3.4.1. Working Condition Parameters

Evaporation Temperature

The cooling capacity and cooling power (SCP) of the MIL-101/20%FLG-water working pair at different evaporation temperatures (10–20 °C) were investigated at an adsorption time of 60 min and desorption time of 60 min. The results are shown in Figure 8.

As seen in Figure 8, the cooling capacity and SCP of the system is 2.14 W and 87.5 W kg⁻¹ at an evaporation temperature of 15 °C, which is 3.06 times that of an evaporation temperature of 10 °C (0.70 W and 28.6 W kg⁻¹). Raising the evaporation temperature to 17 °C and 20 °C, the cooling capacity and SCP of an MIL-101/20%FLG-water working pair just increases by 10.3% and 10%. This is due to the fact that the evaporation pressure of refrigerant (water) rises, and the mass transfer impetus of water on MIL-101/20%FLG increases with the rise of evaporation temperature. Results show that the MIL-101/20%FLG composite is more applicable to an adsorption water chiller application [12,35] with an evaporation temperature of 15–20 °C.
Adsorption Time

The cooling capacity and SCP of an MIL-101/20%FLG-water working pair at different adsorption times (30–300 min) were investigated at an evaporation temperature of 17 °C and desorption time of 60 min. The results are shown in Figure 9.

Seen from Figure 9, the cooling capacity of the system continuously increases with a prolonged adsorption time and reaches up to 2.23–2.40 W at an adsorption time of 90–120 min. The SCP of the system firstly increases and then drops rapidly with the extension of adsorption time. SCP reaches 98.0 W kg\(^{-1}\) under an adsorption time between 90 and 120 min. This is due to the fact that after the initial adsorption stage, the adsorption process of water on MIL-101/20%FLG is mainly in the form of slow capillary condensation in mesoporous cages. The adsorption rate slows down, and the increase in cooling capacity is offset by the extension of adsorption time. Therefore, a reasonable adsorption time of an MIL-101/20%FLG-water working pair is 90–120 min, which is shortened by 25% compared to an MIL-101-water working pair whose optimal adsorption time is 120–180 min (as shown in Figure S5). This is because the removal rate of adsorption heat and cooling rate
are quicker for MIL-101/20%FLG. The adsorption rate of MIL-101/20%FLG for water is relatively increased (as shown in Figure S2).

Compared to the literature [61] (adsorption time of 90–100 min), the adsorption time in this work could be further shortened by optimizing the adsorber configuration to strengthen mass transfer properties.

Desorption Time

The cooling capacity and SCP of MIL-101/20%FLG-water working pairs at different desorption times (20–60 min) were investigated at an evaporation temperature of 17 °C and adsorption time of 90 and 120 min. The results are shown in Figure 10.

As shown in Figure 10, the cooling capacity (a) and SCP (b) rapidly increase below a desorption time of 30 min due to the fast desorption rate, while the cooling capacity of the system is 2.74 W and 2.48 W at adsorption times of 90 min and 120 min, respectively. Prolonging the desorption time to 40 min, the cooling capacity of the system is 2.78 W and 2.49 W at adsorption times of 90 min and 120 min, respectively. However, there is no obvious improvement of cooling capacity at a desorption time greater than 40 min. When desorption time is in the range of 30–40 min, the SCP of the MIL-101/20%FLG-water working pair reaches its maximum of 113.5 W kg⁻¹ at an adsorption time of 90 min. Along with desorption time further increasing, the SCP significantly declines. Therefore, the suitable desorption time of an MIL-101/20%FLG-water working pair is 40 min, which is shortened by 33.3% compared to an MIL-101-water working pair with a desorption time of 60 min (as shown in Figure S6). This is attributed to the higher thermal conduction of MIL-101/20%FLG compared to MIL-101, resulting in a faster heating rate and shorter heating time; thus, the desorption rate is increased and desorption time is decreased.

3.4.2. Adsorption Cooling Performance Comparison of MIL-101/20%FLG-Water and MIL-101-Water Working Pairs

The MIL-101/FLG composite may be more applicable to adsorption water chiller applications with an evaporation temperature of 15–20 °C according to Sections 3.2 and 3.4.1. The cooling performance of MIL-101/20%FLG-water and MIL-101-water working pairs was investigated under typical adsorption water chiller working conditions with an adsorption temperature of 30 °C, evaporation temperature of 16–20 °C, desorption temperatures of 70 °C and 90 °C, condensation temperature of 30 °C, adsorption time of 90 min and desorption time of 30 min. The temperature characteristic curves of the evaporator and
refrigerator are shown in Figure 11, while the results of cooling capacity, SCP and COP are listed in Table 1.

![Figure 11. Temperature characteristic curves of (a) MIL-101-water and (b) MIL-101/20%FLG-water working pairs during the cooling process.](image)

**Table 1.** Cooling capacity, SCP and COP of MIL-101-water and MIL-101/20%FLG-water working pairs for an adsorption water chiller application.

| Working Pair          | Working Conditions                                                                 | Cooling Capacity, W | SCP, W kg⁻¹ | COP  |
|-----------------------|------------------------------------------------------------------------------------|---------------------|--------------|------|
| MIL-101-water         | $T_a = 30\, ^\circ\text{C}$, $T_c = 16–20\, ^\circ\text{C}$, $T_d = 70\, ^\circ\text{C}$ | 1.16                | 46.3         | 0.126|
|                       | $T_a = 30\, ^\circ\text{C}$, $T_c = 30\, ^\circ\text{C}$                         | 1.37                | 54.8         | 0.141|
|                       | $T_a = 30\, ^\circ\text{C}$, $T_c = 16–20\, ^\circ\text{C}$, $T_d = 90\, ^\circ\text{C}$ | 1.77                | 72.2         | 0.187|
| MIL-101/20%FLG-water  | $T_a = 30\, ^\circ\text{C}$, $T_c = 16–20\, ^\circ\text{C}$, $T_d = 70\, ^\circ\text{C}$ | 1.98                | 81.0         | 0.202|
|                       | $T_a = 30\, ^\circ\text{C}$, $T_c = 30\, ^\circ\text{C}$                         |                     |              |      |

$T_a$ = adsorption temperature, $T_c$ = evaporation temperature, $T_d$ = condensation temperature, $T_d$ = desorption temperature.

It is shown in Figure 11 that during the cooling process, the temperature drop of the evaporator and refrigerator for MIL-101/20%FLG-water working pairs is 3.6 °C and 3.3 °C, respectively, which means chilled water of 16–20 °C might be produced.

As seen in Table 1, at desorption temperatures of 70 °C and 90 °C, the cooling capacity, SCP and COP of MIL-101/20%FLG-water working pairs is $1.77–1.98$ W, 72.2–81.0 W kg⁻¹ and 0.187–0.202, respectively, which is 1.43–1.56 times higher than MIL-101-water working pairs. As mentioned above, this is mainly because the thermal conduction of MIL-101 is strengthened, and the heat transfer of an MIL-101 adsorber during the adsorption and desorption process is improved by addition of FLG, which is conducive to reducing the cycle time of water on MIL-101. The results indicate that the cooling performance of MIL-101-water working pairs could be significantly enhanced by adding FLG, and the energy conversion efficiency in adsorption water chiller applications might be improved. This provides a promising adsorbent candidate (MIL-101/FLG composite) in adsorption water chiller applications such as data center cooling, proton exchange membrane fuel cell, automotive engine coolant and vehicle air-conditioning; especially, a better cooling effect would be achieved in the vehicle air-conditioning application (evaporation temperature of 15–20 °C and feasible heat source temperature of 100–130 °C).
3.5. Adsorption Cooling Cyclic Stability and Characterization of MIL-101/20%FLG Composite

3.5.1. Cyclic Stability

The cyclic cooling capacity of an MIL-101/20%FLG-water working pair was investigated at an adsorption temperature of 30 °C, evaporation temperature of 20 °C, desorption temperature of 90 °C, condensation temperature of 30 °C, adsorption time of 90 min and desorption time of 30 min. The result is shown in Figure 12.

![Figure 12](image-url)  
**Figure 12.** Cyclic cooling capacity of an MIL-101/20%FLG-water working pair.

As seen in Figure 12, the cooling capacity of an MIL-101/20%FLG-water working pair is maintained at 1.96–2.01 W after 50 continuous adsorption/desorption cycles.

3.5.2. Characterization of Cycled MIL-101/20%FLG

The XRD patterns of fresh MIL-101/20%FLG and cycled MIL-101/20%FLG are shown in Figure 13, while N₂ adsorption/desorption isotherms and pore structure parameters are shown in Figure 14 and Table 2, respectively.

![Figure 13](image-url)  
**Figure 13.** XRD patterns of fresh MIL-101/20%FLG and cycled MIL-101/20%FLG.
In this work, a novel MIL-101/FLG composite was prepared for improving the thermal conduction performance of MIL-101. The heat transfer characteristic of MIL-101/FLG adsorber was evaluated during adsorption, desorption and cooling process. The adsorption cooling performance of an MIL-101/FLG-water working pair was investigated for typical adsorption water chiller working conditions. The thermal conductivity of the MIL-101/20%FLG composite is 0.8322–0.8603 W m\(^{-1}\) K\(^{-1}\). The heating and cooling rate of the MIL-101/20%FLG adsorber is 2.2 times as much as that of an MIL-101 adsorber; meanwhile, the heating and cooling time is effectively shortened by ~55%. The enhanced heat transfer of an MIL-101/20%FLG adsorber is conducive to the improvement of the cooling performance of MIL-101-water working pairs. Under adsorption water chiller working conditions, the cooling capacity, SCP and COP of an MIL-101/20%FLG-water working pair are 1.77–1.98 W, 72.2–81.0 W kg\(^{-1}\) and 0.187–0.202, respectively. Moreover, the excellent adsorption/desorption cyclic stability of MIL-101/FLG composites is successfully verified. This work provides a reference for improving the heat transfer performance of MOFs and gives a promising material candidate for the MIL-101/FLG composite in research directions.

Figure 14. N\(_2\) adsorption/desorption isotherms of fresh MIL-101/20%FLG and cycled MIL-101/20%FLG.

Table 2. BET surface areas and pore volume of fresh MIL-101/20%FLG and cycled MIL-101/20%FLG.

| Sample                        | BET Surface Area, m\(^2\) g\(^{-1}\) | Total Pore Volume, cm\(^3\) g\(^{-1}\) | Mesopore Volume, cm\(^3\) g\(^{-1}\) | Micropore Volume, cm\(^3\) g\(^{-1}\) |
|-------------------------------|--------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| MIL-101/20%FLG (fresh)        | 1558                                 | 0.85                                   | 0.41                                   | 0.44                                   |
| MIL-101/20%FLG (cycled)       | 1552                                 | 0.84                                   | 0.39                                   | 0.45                                   |
| MIL-101 [37]                 | 2047                                 | 1.12                                   | 0.56                                   | 0.56                                   |

As shown in Figure 13, the major peaks of MIL-101 components are retained in MIL-101/20%FLG, which indicates well the coexistence between FLG and MIL-101. After continuous adsorption cooling cycles, the crystallinity of cycled MIL-101/20%FLG is rarely changed and the phase structure of MIL-101/20%FLG remains stable.

It is shown in Figure 14 that the N\(_2\) adsorption uptake of cycled MIL-101/20%FLG and fresh MIL-101/20%FLG is similar. Seen from Table 2, the BET surface area of fresh MIL-101/20%FLG is decreased by 23.9%, and the pore volume is reduced by 24.1%, compared to MIL-101 [37], which is consistent with the adding proportion of FLG. MIL-101 is not significantly destructed by the addition of FLG. After continuous adsorption and desorption cycles, the porous structure of cycled MIL-101/20%FLG is similar to fresh MIL-101/20%FLG.

4. Conclusions

In this work, a novel MIL-101/FLG composite was prepared for improving the thermal conduction performance of MIL-101. The heat transfer characteristic of MIL-101/FLG adsorber was evaluated during adsorption, desorption and cooling process. The adsorption cooling performance of an MIL-101/FLG-water working pair was investigated for typical adsorption water chiller working conditions. The thermal conductivity of the MIL-101/20%FLG composite is 0.8322–0.8603 W m\(^{-1}\) K\(^{-1}\). The heating and cooling rate of the MIL-101/20%FLG adsorber is 2.2 times as much as that of an MIL-101 adsorber; meanwhile, the heating and cooling time is effectively shortened by ~55%. The enhanced heat transfer of an MIL-101/20%FLG adsorber is conducive to the improvement of the cooling performance of MIL-101-water working pairs. Under adsorption water chiller working conditions, the cooling capacity, SCP and COP of an MIL-101/20%FLG-water working pair are 1.77–1.98 W, 72.2–81.0 W kg\(^{-1}\) and 0.187–0.202, respectively. Moreover, the excellent adsorption/desorption cyclic stability of MIL-101/FLG composites is successfully verified. This work provides a reference for improving the heat transfer performance of MOFs and gives a promising material candidate for the MIL-101/FLG composite in research directions.
for adsorption water chillers (16–20 °C), including data center cooling, liquid cooling of proton exchange membrane fuel cell, automotive engine coolant and especially vehicle air-conditioning. It is foreseeable that the overall heat transfer and cooling capacity of MIL-101/FLG-water working pairs can be further improved in a new adsorption cooling device configuration.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/en14164970/s1, Figure S1: Adsorption isotherms of water on MIL-101 and MIL-101/20%FLG composite, Figure S2: Adsorption rate curves of water on MIL-101 and MIL-101/20%FLG composite, Figure S3: TG-DTA curves of water on MIL-101/20%FLG composite, Figure S4: XRD pattern (a), SEM image (b) and Raman spectra (c) of FLG, Figure S5: Effect of adsorption time on cooling capacity and cooling power of MIL-101-water working pair, Figure S6: Effect of desorption time on cooling capacity (a) and cooling power (b) of MIL-101-water working pair.

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**Nomenclature**

- **SCP** specific cooling power [W kg⁻¹]
- **COP** coefficient of performance
- **Qₜ** cooling capacity per unit of cycle time [W]
- **Δmad** cyclic water amount [kg]
- **ΔHe** latent heat of vaporization [kJ kg⁻¹]
- **m** mass [kg]
- **Qₑvap** evaporative cooling capacity [kJ]
- **Qᵢnput** heat absorbed during desorption process [kJ]
- **hₜ** desorption enthalpy [kJ kg⁻¹]
- **T** temperature of adsorber [°C]
- **Δt** cycle time [s]
- **wt** mass fraction [%]
- **y** result calculated from the measured data
- **vᵢ** measured data
- **Δvᵢ** measurement error
- **P** vapor pressure [Pa]
- **Eₜ** desorption activation energy [kJ mol⁻¹]
- **φ** heating rate [°C min⁻¹]
- **R** gas constant [8.314 J mol⁻¹ °C⁻¹]
- **Δx** cyclic water amount per unit mass of adsorbents [kg kg⁻¹]

**Subscript:**
- **ads** adsorbent
- **c** capacity
- **s** saturated
- **d** desorption
- **M** Middle
- **evap** evaporation
References

1. Alahmer, A.; Ajib, S. Solar cooling technologies: State of art and perspectives. *Energy Convers. Manag.* 2020, 214, 112896. [CrossRef]

2. Allouhi, A.; Kousksou, T.; Jamil, A.; El Rhafiki, T.; Mourad, Y.; Zeraouli, Y. Optimal working pairs for solar adsorption cooling applications. *Energy* 2015, 79, 235–247. [CrossRef]

3. Choudhury, B.; Saha, B.; Chatterjee, P.K.; Sarkar, J.P. An overview of developments in adsorption refrigeration systems towards a sustainable way of cooling. *Appl. Energy* 2013, 104, 554–567. [CrossRef]

4. Deng, J.; Wang, R.; Han, G. A review of thermally activated cooling technologies for combined cooling, heating and power systems. *Prog. Energy Combust. Sci.* 2011, 37, 172–203. [CrossRef]

5. Shabir, F.; Sultan, M.; Miyazaki, T.; Saha, B.B.; Askalany, A.; Ali, D.I.; Zhou, Y.; Ahmad, R.; Shamshiri, R.R. Recent updates on the adsorption capacities of adsorbent-adsorbate pairs for heat transformation applications. *Renew. Sustain. Energy Rev.* 2019, 119, 109630. [CrossRef]

6. Wang, J.; Hu, E.; Blazewicz, A.; Ezzat, A.W. Simulation of accumulated performance of a solar thermal powered adsorption refrigeration system with daily climate conditions. *Energy* 2018, 165, 487–498. [CrossRef]

7. Habib, K.; Saha, B.; Koyama, S. Study of various adsorbent–refrigerant pairs for the application of solar driven adsorption cooling in tropical climates. *Appl. Therm. Eng.* 2014, 72, 266–274. [CrossRef]

8. Wu, W.; Zhang, X.; Li, X.; Shi, W.; Wang, B. Comparisons of different working pairs and cycles on the performance of adsorption heat pump for heating and domestic hot water in cold regions. *Appl. Therm. Eng.* 2012, 48, 349–358. [CrossRef]

9. Liu, Y.; Wang, R.; Xia, Z. Experimental performance of a silica gel–water adsorption chiller. *Appl. Therm. Eng.* 2005, 25, 359–375. [CrossRef]

10. Manila, M.R.; Mitra, S.; Dutta, P. Studies on dynamics of two-stage air cooled water/silica gel adsorption system. *Appl. Therm. Eng.* 2020, 178, 115552. [CrossRef]

11. Pan, Q.; Peng, J.; Wang, H.; Sun, H.; Wang, R. Experimental investigation of an adsorption air-conditioner using silica gel-water working pair. *Sol. Energy* 2019, 185, 64–71. [CrossRef]

12. Pan, Q.; Peng, J.; Wang, R. Experimental study of an adsorption chiller for extra low temperature waste heat utilization. *Appl. Therm. Eng.* 2019, 163, 114341. [CrossRef]

13. Wang, D.C.; Wu, J.Y.; Xia, Z.Z.; Zhai, H.; Wang, R.Z.; Dou, W.D. Study of a novel silica gel-water adsorption chiller. Part II. Experimental study. *Int. J. Refrig.* 2005, 28, 1084–1091. [CrossRef]

14. Younes, M.M.; El-Sharkawy, I.I.; Kaboeel, A.E.; Uddin, K.; Pal, A.; Mitra, S.; Thu, K.; Saha, B.B. Synthesis and characterization of silica gel composite with polymer binders for adsorption cooling applications. *Int. J. Refrig.* 2018, 98, 161–170. [CrossRef]

15. Brancato, V.; Frazzica, A. Characterisation and comparative analysis of zeotype water adsorbents for heat transformation applications. *Sol. Energy Mater. Sol. Cells* 2018, 180, 91–102. [CrossRef]

16. Du, S.W.; Li, X.H.; Yuan, Z.X.; Du, C.X.; Wang, W.C.; Liu, Z.B. Performance of solar adsorption re-frigeration in system of SAPO-34 and ZSM-5 zeolite. *Sol. Energy* 2016, 138, 98–104. [CrossRef]

17. Teo, H.W.B.; Chakraborty, A.; Han, B. Water adsorption on CHA and AFI types zeolites: Modelling and investigation of adsorption chiller under static and dynamic conditions. *Appl. Therm. Eng.* 2017, 127, 35–45. [CrossRef]

18. Myat, A.; Choon, N.K.; Thu, K.; Kim, Y-D. Experimental investigation on the optimal performance of Zeolite–water adsorption chiller. *Appl. Energy* 2013, 102, 582–590. [CrossRef]

19. Wang, D.; Xia, Z.; Wu, J. Design and performance prediction of a novel zeolite–water adsorption air conditioner. *Energy Convers. Manag.* 2006, 47, 590–610. [CrossRef]

20. Al-Dadah, R.; Mahmoud, S.; Elsayed, E.; Youssef, P.; Al-Mousawi, F. Metal-organic framework mate-rials for adsorption heat pumps. *Energy* 2020, 190, 116356. [CrossRef]

21. Al-Mousawi, E.N.; Al-Dadah, R.; Mahmoud, S. Low grade heat driven adsorption system for cooling and power generation using advanced adsorbent materials. *Energy Convers. Manag.* 2016, 126, 373–384. [CrossRef]

22. Ehrenmann, J.; Henninger, S.K.; Janiak, C. Water adsorption characteristics of MIL-101 for heat-transformation applications of MOFs. *Eur. J. Inorg. Chem.* 2011, 4, 471–474. [CrossRef]

23. Henninger, S.K.; Habib, H.A.; Janiak, C. MOFs as Adsorbents for Low Temperature Heating and Cooling Applications. *J. Am. Chem. Soc.* 2009, 131, 2776–2777. [CrossRef]

24. Solovyeva, M.V.; Gordeeva, L.G.; Krieger, T.A.; Aristov, Y.I. MOF-801 as a promising material for ad-sorption cooling: Equilibrium and dynamics of water adsorption. *Energy Convers. Manag.* 2018, 174, 356–363. [CrossRef]

25. He, F.; Nagano, K.; Togawa, J. Experimental study and development of a low-cost 1 kW adsorption chiller using composite adsorbent based on natural mesoporous material. *Energy* 2020, 209, 118365. [CrossRef]

26. He, Z.; Bai, Y.; Huang, H.; Li, J.; Huheitaoli; Kobayashi, N.; Osaka, Y.; Deng, L. Study on the performance of compact adsorption chiller with vapor valves. *Appl. Therm. Eng.* 2017, 126, 37–42. [CrossRef]

27. Jiao, K.; Li, X. Water transport in polymer electrolyte membrane fuel cells. *Prog. Energy Combust. Sci.* 2011, 37, 221–291. [CrossRef]

28. Gao, J.; Wang, L.W.; Tian, Y.C. Numerical and experimental investigation of multi-halide chemisorp-tion system for exhaust gas heat recycling. *Appl. Therm. Eng.* 2021, 194, 117–118. [CrossRef]

29. Vasta, S.; Frene, A.; Sapienza, A.; Costa, F.; Restuccia, G. Development and lab-test of a mobile adsorption air-conditioner. *Int. J. Refrig.* 2012, 35, 701–708. [CrossRef]
30. Zimmermann, S.; Meijer, I.; Tiwari, M.; Paredes, S.; Michel, B.; Poulilikakos, D. Aquasar: A hot water cooled data center with direct energy reuse. *Energies* 2012, 43, 237–245. [CrossRef]
31. Laurenz, E.; Füldner, G.; Schnabel, L.; Schmitz, G. A Novel Approach for the Determination of Sorption Equilibria and Sorption Enthalpy Used for MOF Aluminium Fumurate with Water. *Energies* 2020, 13, 3003. [CrossRef]
32. Elsayed, E.; Al-Dadah, R.; Mahmoud, S.; Anderson, P.A.; Elsayed, A.; Youssef, P.G. CPO-27(Ni), alu-minium fumurate and MIL-101(Cr) MOF materials for adsorption water desalination. *Desalination* 2017, 406, 25–36. [CrossRef]
33. Khutia, A.; Rammelberg, H.U.; Schmidt, T.; Henninger, S.K.; Janiak, C. Water sorption cycle measurements on functionalized MIL-101Cr for heat transformation application. *Chem. Mater.* 2013, 25, 790–798. [CrossRef]
34. Elsayed, E.; Wang, H.Y.; Anderson, P.A.; Al-Dadah, R.; Mahmoud, S.; Navarro, H.; Ding, Y.L.; Bowen, J. Development of MIL-101(Cr)/GrO composites for adsorption heat pump applications. *Micropor. Mesopor. Mat.* 2017, 244, 180–191. [CrossRef]
35. Gordeeva, I.G.; Tu, Y.D.; Pan, Q.; Palash, M.; Saha, B.B.; Aristov, Y.I.; Wang, R.Z. Metal-organic frameworks for energy conversion and water harvesting: A bridge between thermal engineering and material science. *Nano Energy* 2021, 84, 105946. [CrossRef]
36. Rui, Z.; Li, Q.; Cui, Q.; Wang, H.; Chen, H.; Yao, H. Adsorption Refrigeration Performance of Shaped MIL-101-Water Working Pair. *Chin. J. Chem. Eng.* 2014, 22, 570–575. [CrossRef]
37. Ma, L.; Wu, Q.; Yang, H.; Yin, Y.; Liu, Z.; Cui, Q.; Wang, H. Performance evaluation of shaped MIL-101–ethanol working pair for adsorption refrigeration. *Appl. Therm. Eng.* 2015, 95, 223–228. [CrossRef]
38. Xu, Z.; Yin, Y.; Shao, J.; Liu, Y.; Zhang, L.; Cui, Q.; Wang, H. Study on heat transfer and cooling performance of copper foams cured MIL-101 adsorption unit tube. *Energy* 2019, 191, 116302. [CrossRef]
39. Chen, H.; Cui, Q.; Gu, C.H.; Yao, H.Q. Heat enhancement of adsorbents in adsorption refrigeration system. *J. Nanjing Tech Univ.* 2004, 26, 13–18.
40. Hu, P.; Yao, J.J.; Chen, Z.S. Analysis for composite zeolite/foam aluminum–water mass recovery adsorption refrigeration system driven by engine exhaust heat. *Energ. Convers. Manag.* 2009, 50, 255–261. [CrossRef]
41. Mohammed, R.H.; Mesalhy, O.; Elsayed, M.L.; Chow, L.C. Performance enhancement of adsorption beds with silica-gel particles packed in aluminum foams. *Int. J. Refrig.* 2014, 38, 201–212. [CrossRef]
42. Chen, K.; Chao, C.Y.; Wu, C. Measurement of properties and performance prediction of the new MWCNT-embedded zeolite 13X/CaCl2 composite adsorbents. *Int. J. Heat Mass Transf.* 2015, 89, 308–319. [CrossRef]
43. Eun, T.H.; Song, H.K.; Han, J.H.; Lee, K.H.; Kim, J.N. Enhancement of heat and mass transfer in silica-expanded graphite composite blocks for adsorption heat pumps: Part I. Characterization of the composite blocks. *Int. J. Refrig.* 2000, 23, 64–73. [CrossRef]
44. Eun, T.H.; Song, H.K.; Han, J.H.; Lee, K.H.; Kim, J.N. Enhancement of heat and mass transfer in silica-expanded graphite composite blocks for adsorption heat pumps. Part II. Cooling system using the composite blocks. *Int. J. Refrig.* 2000, 23, 74–81. [CrossRef]
45. Wu, W.D.; Wang, C.; Meng, X.W.; Zhang, H. Physical properties and refrigeration performance of compound adsorbent composed of additive and zeolite molecular sieve. *Chem. Ind. Eng. Pro.* 2016, 35, 692–699.
46. Bahreman, H.; Ahmad, M.; Bahrami, M. Analytical modeling of oscillatory heat transfer in coated sorption beds. *Int. J. Heat Mass Transf.* 2018, 121, 1–9. [CrossRef]
47. Bahreman, H.; Khajehpour, M.; Bahrami, M. Finding optimal conductive additive content to enhance the performance of coated sorption beds: An experimental study. *Appl. Therm. Eng.* 2018, 143, 308–315. [CrossRef]
48. Pal, A.; Uddin, K.; Rocky, K.A.; Thu, K.; Saha, B.B. CO2 adsorption onto activated carbon–graphene composite for cooling applications. *Int. J. Refrig.* 2019, 106, 558–569. [CrossRef]
49. Pal, A.; Uddin, K.; Thu, K.; Saha, B.B. Activated carbon and graphene nanoplatelets based novel composite for performance enhancement of adsorption cooling cycle. *Energy Convers. Manag.* 2018, 180, 134–148. [CrossRef]
50. Yang, S.; Kim, H.; Narayanan, S.; McKay, I.S.; Wang, E.N. Dimensionality effects of carbon-based thermal additives for microporous adsorbents. *Mater. Des.* 2015, 85, 520–526. [CrossRef]
51. Nika, D.L.; Balandin, A.A. Phonons and thermal transport in graphene and graphene-based materials. *Rep. Prog. Phys.* 2017, 80, 036502. [CrossRef] [PubMed]
52. Ghosh, S.K.; Calizo, I.; Teweldebrhan, D.; Poktilov, E.P.; Nika, D.; Balandin, A.A.; Bao, W.; Miao, F.; Lau, C.N. Extremely high thermal conductivity of graphene: Prospects for thermal management applications in nanoelectronic circuits. *Appl. Phys. Lett.* 2008, 92, 151911. [CrossRef]
53. Ghosh, S.; Bao, W.; Nika, D.L.; Subrina, S.; Poktilov, E.P.; Lau, C.N.; Balandin, A.A. Dimensional crossover of thermal transport in few-layer graphene. *Nat. Mater.* 2010, 9, 555–558. [CrossRef] [PubMed]
54. Balandin, A.A. Phononics of Graphene and Related Materials. *ACS Nano* 2020, 14, 5170–5178. [CrossRef]
55. Ma, L.; Yang, H.; Wu, Q.; Yin, Y.; Liu, Z.; Cui, Q.; Wang, H. Study on adsorption refrigeration performance of MIL-101-isobutane working pair. *Energy* 2015, 93, 786–794. [CrossRef]
56. Yin, Y.; Shao, J.; Zhang, L.; Cui, Q.; Wang, H. Study on heat conduction and adsorption/desorption characteristic of MIL-101/few layer graphene composite. *J. Porous Mater.* 2021, 28, 1197–1213. [CrossRef]
57. Gustafsson, S.E. Transient plane source techniques for thermal conductivity and thermal diffusivity measurements of solid materials. *Rev. Sci. Instrum.* 1991, 62, 797–804. [CrossRef]
58. Al-Ajlan, S.A. Measurements of thermal properties of insulation materials by using transient plane source technique. *Appl. Therm. Eng.* 2006, 26, 2184–2191. [CrossRef]

59. Cui, Q.; Tao, G.; Chen, H.; Guo, X.; Yao, H. Environmentally benign working pairs for adsorption refrigeration. *Energy* 2005, 30, 261–271. [CrossRef]

60. Wang, R.Z.; Wang, L.W.; Wu, J.Y. *Theory and its Application of Adsorption Refrigeration*; China Science Publishing House: Beijing, China, 2007.

61. Liu, Z.; Zhao, B.; Zhu, L.; Lou, F.; Yan, J. Performance of MIL-101(Cr)/Water Working Pair Adsorption Refrigeration System Based on a New Type of Adsorbent Filling Method. *Materials* 2020, 13, 195. [CrossRef] [PubMed]