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Numerical investigation of MIL-101(Cr)/GrO composite performance in adsorption cooling systems

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Abstract

MIL-101(Cr)/graphene oxide composites were investigated for the application of adsorption cooling. Two composites with two different synthesis techniques were chosen, 2%GrO_syn and 5%GrO_phys, owing to the superior water adsorption uptake of the first and the high thermal conductivity of the latter. The thermodynamic cycle performance of a two-bed adsorption system was evaluated using Simulink software to assess the performance of each composite. Under the operating conditions investigated, the 2%GrO_synthesis composite showed a similar specific cooling power (SCP) and coefficient of performance (COP) to the MIL-101(Cr) system with no change in cycle time and with a lower desorption temperature of 90°C. The 5%GrO_phys composite showed a decreased SCP and an increased COP at the same cycle time. Nevertheless, the desorption temperature of such system decreased from 100°C for the neat material to only 80°C. This highlights the potential of such composites in more efficient adsorption heat pump systems.

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Keywords: Metal–organic framework; composite; adsorption; heat pump; cooling; thermal conductivity.

1. Introduction

In adsorption heat pumps, a working fluid is evaporated, taking its evaporation heat from the surroundings and thereby producing useful cold in cooling applications. Then vapour is adsorbed into a porous material, generating adsorption heat. This heat is released to the environment in cooling cases or produces useful heat in heat pump applications. During the desorption process, the porous material is regenerated by introducing heat from various external heat sources like solar energy or industrial waste heat. Finally, the desorbed fluid is condensed at a medium temperature level, releasing the heat of condensation. This heat is useful in the heat pump application and is released to the environment in cooling applications [1]. Silica gel and zeolites have been extensively studied due to their

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adsorption affinity, availability and status as environmentally friendly adsorbents. Such systems usually use water as an adsorbate due to its high latent heat of vaporization and non-toxicity; but one of the main drawbacks in these adsorption systems is the poor heat transfer properties in the bed and the low thermal conductivity of the porous materials, limiting the ability of the heat transfer processes to reach the desired operating temperatures quickly during both the adsorption and desorption phases. Previous studies proposed that the overall thermal conductivity can be improved through using different adsorption bed designs with a high contact heat transfer area, which can be done through using a fin and tube design or adsorbent-coated heat exchangers. Many studies investigated the design parameters and their effect on the performance of the system while others proposed improving the thermal properties of the adsorbent material itself through introducing metal pieces or expanded graphite.

In the present work, two composites of porous metal-organic framework (MOF) MIL-101(Cr) and graphene oxide were synthesized. Detailed preparation procedures of the composites can be found elsewhere [2]. The first composite 2%GrO_syn showed an improved water vapour uptake while the 5%GrO_phys composite showed a significant enhanced thermal conductivity compared to the parent MIL-101(Cr) [2]. The performance of the two composites and the neat MIL-101(Cr) material was assessed through a Simulink model of two adsorption fin–tube beds. This study shows that the 2%GrO_syn composite showed improved SCP and COP compared to the neat material while the 5%GrO_phys showed a decreased SCP but an enhanced COP.

Nomenclature

A	Adsorption potential	$J.mol^{-1}$
E	Adsorption characteristic parameter	$J.mol^{-1}$
E_a	Activation energy	$J.mol^{-1}$
K_0	LDF model empirical constant	s^{-1}
M	Mass	kg
$\dot{m}$	Mass flow rate	$kg\cdot s^{-1}$
P	Pressure	kPa
P_s	Saturation pressure of adsorbate at adsorption temperature	kPa
Q_{st}	Isosteric heat of adsorption	$J.kg^{-1}$
R	Ideal gas constant	$J.(mol.K)^{-1}$
SCP	Specific Cooling Power	$W\cdot kg^{-1}$
T	Temperature	K
t	time	s
x	Equilibrium uptake	$g_{H2O}.g_{ads}{}^{-1}$
x_0	Maximum uptake	$g_{H2O}.g_{ads}{}^{-1}$

Subscripts

ads	Adsorption
cond	Condenser
des	Desorption
evap	Evaporator
HF	Heating fluid
in	Inlet
out	Outlet
ref	Refrigerant

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2. Water adsorption characteristics

Fig.1a shows the measured water adsorption isotherms of the neat material and the two composites at 25°C. The MIL-101(Cr) and its composites exhibited type IV isotherm. At low relative pressure (≤ 0.4), the limited water uptake is related to the dominant effect of the hydrophobicity of the organic linker. At higher relative pressure (0.4–0.5), a steep increase in the water uptake takes place due to capillary condensation which usually takes place in mesoporous materials. At high relative pressure (≥ 0.5), the pores are almost filled exhibiting a stable uptake. Also, it can be observed that the 5%GrO_phys composite has a lower water vapour uptake than the neat material, which may be attributed to the low uptake of GrO in addition to other factors such as lower crystallinity and potential pore blocking by the GrO. The 2%GrO_syn composite showed a slightly higher water vapour uptake in the high relative pressure range. This may be attributed to the new pores created at the interface of the MIL structure and the graphene layers perhaps through the coordination of the oxygen functionalities of GrO to the metallic centers of the MIL-101(Cr) structure [2]. Fig.1b shows the measured water adsorption isotherms at 15°C and 35°C.

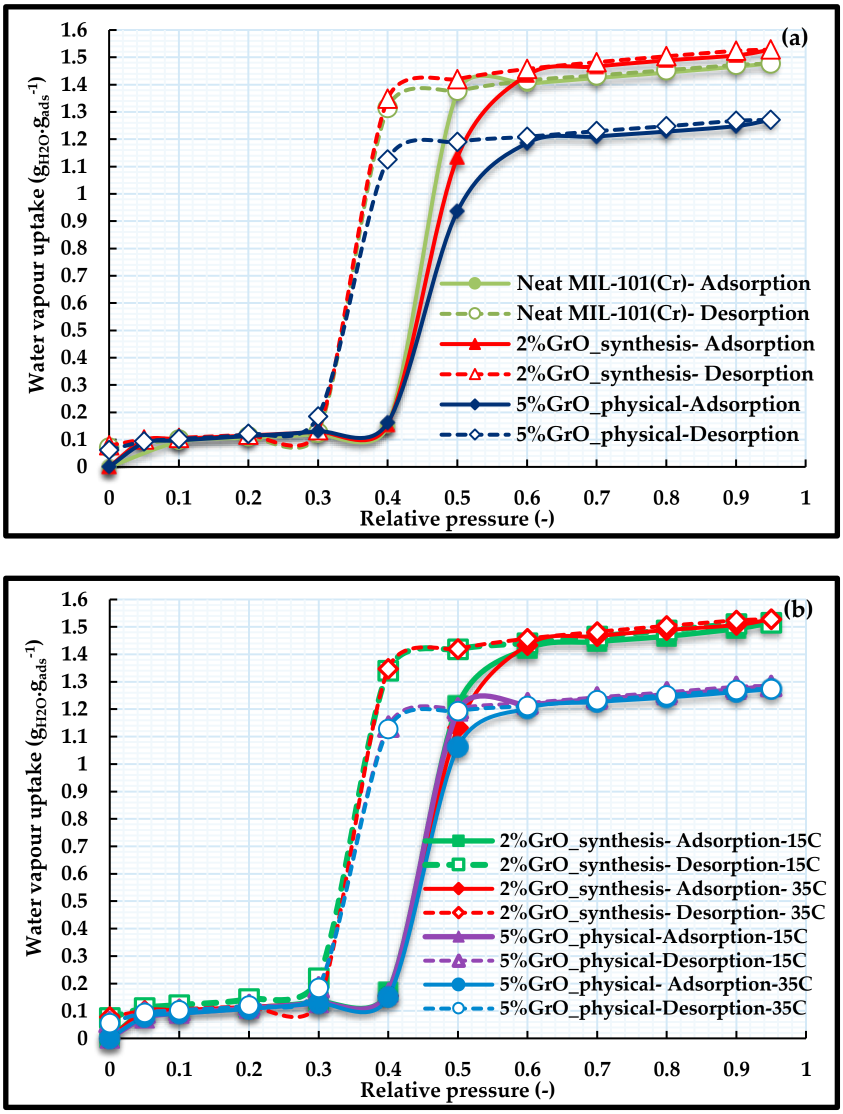

Fig. 1 a. Measured water adsorption isotherms of 2%GrO_syn and 5%GrO_phys composites at 25°C and b. measured water adsorption isotherms at 15°C and 35°C.

3. Adsorption isotherms and kinetics models:

The isotherm models of MIL-101(Cr), 2%GrO_syn and 5%GrO_phys, were developed in terms of the adsorption potential (Eq. 1) to examine the effect of temperature on the adsorption capacity.

$$A = -RT\ln\left(\frac{P}{P_s}\right) \tag{1}$$

The developed equations were used to predict the water uptake at a wide range of operating conditions.
The adsorption isotherms of MIL-101(Cr) were fitted using Eq. 2–5:

$$x = 0.424\exp(-0.00028A) \qquad \mathbf{A > 3900} \tag{2}$$

$$x = 0.463 - 0.00024A + 5.4E-8A^2 - 4.06E-12A^3 \qquad \mathbf{2200 \le A \le 3900} \tag{3}$$

$$x = 2.92\ \mathrm{E23}\left(\mathrm{A}^{-7.25}\right) \qquad \mathbf{1700 < A < 2200} \tag{4}$$

$$x = 1.51 - 0.000266A + 0.363E-6A^2 - 0.177E-9A^3 \qquad \mathbf{A \le 1700} \tag{5}$$

The 2%GrO_syn composite isotherms were measured at 15°C, 25°C and 35°C which were fitted using Eq. 6–8:

$$x = 1.77(A^{-0.33}) \qquad \mathbf{A \ge 2800} \tag{6}$$

$$x = 177.276 - 0.54\mathrm{A} + 0.00064\mathrm{A}^2 - 3.73\mathrm{E}-7\mathrm{A}^3 + 1.06\mathrm{E}-10\mathrm{A}^4 - 1.17\mathrm{E}-14\mathrm{A}^5 \qquad \mathbf{1200 < A < 2000} \tag{7}$$

$$x = 1.533 - 0.00008A \qquad \mathbf{A \le 1200} \tag{8}$$

The 5%GrO_phys composite adsorption isotherms were also measured at 15°C, 25°C and 35°C and fitted using Eq. (9–11):

$$x = 13.036(A^{-0.574}) \qquad \mathbf{A \ge 2100} \tag{9}$$

$$x = -477.607 + 0.967A - 0.00072.A^2 + 0.00000024A^3 - 2.92E11A^4 \qquad \mathbf{1900 \le A < 2100} \tag{10}$$

$$x = -0.000064A + 1.28 \qquad \mathbf{A < 1900} \tag{11}$$

The rate of adsorption (adsorption kinetics) is another crucial parameter determining the residence time required for the completion of the adsorption cycle. A linear driving force model was chosen to describe the adsorption rate as it has been widely known for being simple, analytical and physically consistent [3]. Eq. 12 represents the LDF model. Table 1 gives the values of parameters E_a and K_0.

$$\frac{dx}{dt} = K_0.\exp\left(-\frac{E_a}{R.T}\right).(x - x_0) \tag{12}$$

Table 1 Values of the parameters E_a and K_0.

	E_a	K_0
MIL-101(Cr) **2%GrO_syn** **5%GrO_phys**	27722	9.374

4. Dynamic modelling of the adsorption system:

The adsorption system was simulated by Simulink-Matlab to compare the performance of the MIL-101(Cr)/GrO composites and then investigate the effect of different operating conditions. The adsorption system in this study consisted of an evaporator, a condenser and a fin–tube adsorption bed. The region between the two fins is packed with the adsorbent material. A fully developed turbulent fluid was assumed, and the convection coefficient between the tube and fluid is calculated using the Dittus-Boelter equation. The materials of the tube and fin are both copper and the region between the two fins is covered with the adsorbent.

Eq. 13–15 describe the mass and heat balance equations of the adsorption / desorption phases.

The overall mass balance recirculated in the evaporator:

$$\frac{dM_{ref,evap}}{dt} = -M_{ads}\frac{dx_{des}}{dt} - M_{ads}\frac{dx_{ads}}{dt} \tag{13}$$

The adsorption/desorption temperature was predicted using the energy balance as:

$$\left(M_{ads}(C_{p_{ads}} + xC_{p_{ref,v}}) + M_{cu,ads}C_{p_{cu,ads}}\right)\frac{dT_{ads}}{dt} = M_{ads}Q_{st}\frac{dx}{dt} + \dot{m}_{HF}C_{p_{HF}}(T_{HF,in} - T_{HF,out}) \tag{14}$$

The outlet heat source/cooling medium are calculated from the logarithmic mean temperature:

$$T_{HF,out} = T_{ads} + \left(T_{HF,in} - T_{ads}\right)\exp\left(-\frac{U_{ads}A_{ads}}{\dot{m}_{HF}C_{p_{HF}}}\right) \tag{15}$$

To assess the performance of the system, the coefficient of performance (COP) and the specific cooling capacity (SCP) were calculated through Eq. 16–17:

$$COP = \frac{Q_{eva}}{Q_{des}} \tag{16}$$

$$SCP = \frac{Q_{eva}}{M_{ads}.t_{cycle}} \tag{17}$$

5. Results and discussion:

The effect of evaporation temperature on the performance of the three materials was investigated through changing the evaporation temperature from 10°C to 15°C which are typically used for air conditioning systems and then to a higher evaporation temperature of 20°C which can be used in moderate or high temperature cooling systems. Fig.2a shows the optimum half cycle time of the neat MIL-101(Cr), the 2%GrO_syn and the 5%GrO_phys composites under the specified operating conditions. At evaporation temperatures of 10°C and 15°C, all the materials had an optimum half cycle time of 2000 s. The 2%GrO_syn and 5%GrO_phys composites showed slightly lower SCP values compared to the neat MIL-101(Cr). The low values of the SCP may be attributed to the low adsorption rate in the low relative pressure range as evaporation temperatures of 10°C and 15°C correspond to working relative pressures of 0.3 and 0.4, respectively. Regarding the COP of the systems and from Fig. 2b, the 5%GrO composite showed the highest COP which may be attributed to the improvement in the thermal conductivity leading to lowering of the desorption heat required. The low values of SCP and COP for the three systems may be attributed to the low concentration of the circulated refrigerant and low adsorbent to metal mass ratio [5]. As previously shown in Fig.1, the neat MIL-101(Cr) and the two composites exhibit type IV adsorption isotherms, which means that their performance depends significantly on the evaporation temperature and increases markedly by increasing it [1]. The effect of increasing the evaporation temperature to 20°C on the system performance at the optimum desorption temperatures is illustrated in Fig.3. At an evaporation temperature of 20°C, the 2%GrO_syn composite showed a higher SCP and a slightly higher COP than the neat material, while it showed a lower desorption temperature of 90°C. Such performance is attributed to the fact that the 2% GrO composite surpassed the neat material at relative pressures higher than 0.5. A lower SCP was observed for the 5%GrO composite which may be attributed to the lower adsorption rate. Nevertheless, the 5%GrO_phy system showed an improved COP with decreasing the desorption temperature from 100°C to 80°C. Also, it can be noticed that as the evaporation temperature increased, the optimum time increased from 2000 s to 3500 s. Comparing Fig. 2 to Fig. 3, it is evident that increasing the evaporation temperature from 10°C or 15°C to 20°C would significantly increase the SCP and COP of the three systems.

6. Conclusions

Under the operating conditions investigated, introducing GrO to MIL-101(Cr) in the 2%GrO_syn composite resulted in increased water uptake in the high relative pressure range with enhanced thermal conductivity. The 5%GrO_phys composite showed a reduced SCP but a significant enhancement in COP. Also, a significant decrease in desorption temperature was observed for the 2%GrO_syn and the 5%GrO_phys composites as they decreased from 100°C for MIL-101(Cr) to 90°C and 80°C, respectively. This proves the potential of the MIL-101(Cr)/GrO composites in adsorption cooling/heat pump applications and also how important this information is in designing the best adsorption system for suitable operating conditions.

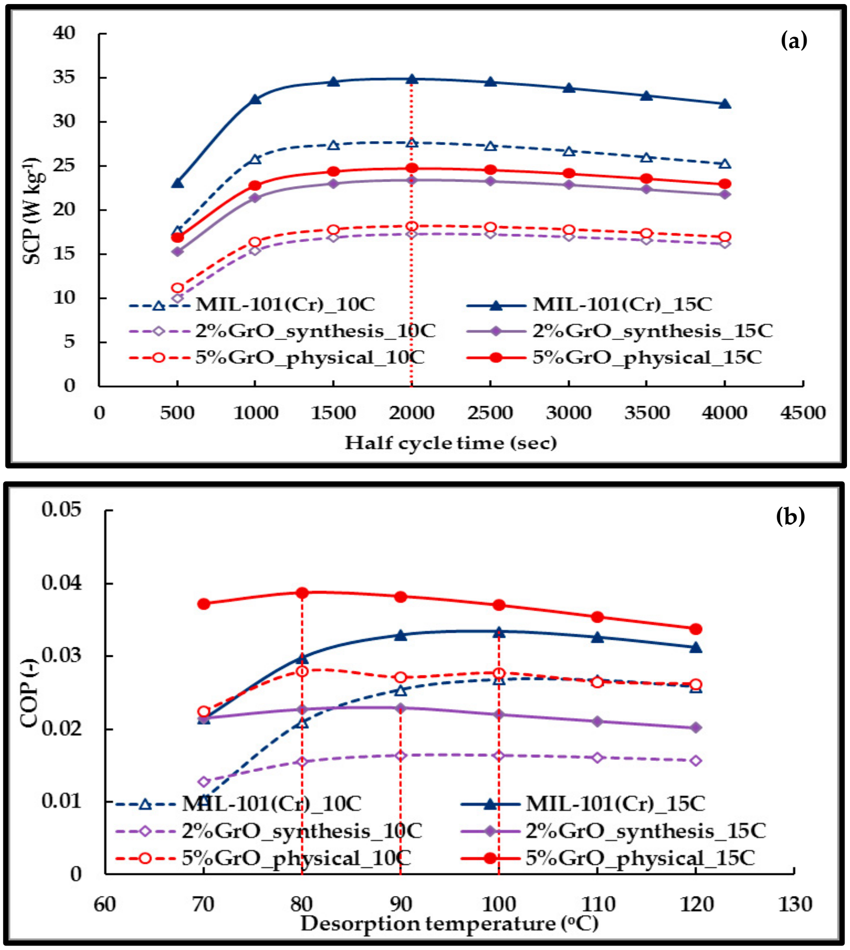

Fig. 2 a. Optimum half cycle time (vertical dotted red line) and b. optimum desorption temperatures (vertical dotted red lines) for MIL-101(Cr), 2%GrO_syn and 5%GrO_phys composites.

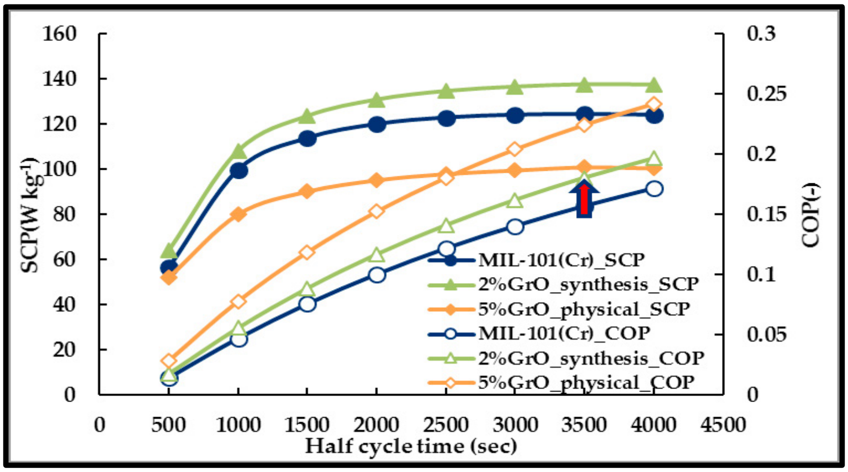

Fig. 3 Optimum half cycle time for MIL-101(Cr), 2%GrO_syn and 5%GrO_phys composites at an evaporation temperature of 20°C (at optimum desorption temperatures).

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