NUMERICAL STUDY ON THE PERFORMANCE OF ADSORPTION REFRIGERATION SYSTEM WITH FINNED BED STRUCTURE PAIRED WITH MOF-WATER AS WORKING FLUID

by

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A single-bed finned tube adsorption refrigeration system model was established to compare the adsorption characteristics of three metal organic framework materials, MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/ $CaCl_2$-20%. The change of material properties under different thickness/length/number of fins was characterized, and the most suitable adsorption bed structure for different materials was obtained. The results show that the number of fins has little effect on the COP and specific cooling power of the material in the system. Choosing thinner fins can improve the COP of the system. With the increase of fin height, the COP showed a trend of increasing first and then decreasing. The three materials, MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20%, obtained the highest COP when the fin heights were 50 mm, 60 mm, and 70 mm, respectively. The maximum specific cooling power was obtained when the fin heights were 20 mm, 60 mm, and 70 mm, which were 21.7 W/kg, 90.1 W/kg, and 174.5 W/kg, respectively. The height of the fin has a great influence on the performance of the system. When designing the adsorption bed, the appropriate fin height should be selected for the specific adsorbent.

Key words: *adsorption, adsorbent, MIL-101(Cr), performance, simulation*

Introduction

The total number of refrigeration, air conditioning, and heat pump systems in operation worldwide is about 5 billion, and the refrigeration industry consumes 20% of the world's total electricity consumption [1]. New refrigerants that replace Freon and energy-saving and environmentally-friendly refrigeration technologies are an urgent need for sustainable development. The refrigerant of adsorption refrigeration is generally with zero ozone depletion potential and global warming potential [2]. However, the shortcomings of traditional adsorbents hinder the development of adsorption refrigeration [3].

In recent years, there have been a lot of theoretical and experimental studies on the selection of new adsorption working pairs and the improvement of system performance in adsorption refrigeration systems. Asif Sha and Baiju [4] presented a thermodynamic model for analysing the performance of a two-bed solar adsorption cooling system which used activated carbon/ethanol as the working pair. Baiju *et al.* [5] established the thermodynamic model of

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adsorption refrigeration as well as the energy-exergy analysis used MATLAB R2019b platform, the working pair was also activated carbon/ethanol. But ethanol is flammable and volatile. Water is non-toxic, non-flammable, non-volatile, easily available and has a high latent heat of evaporation, it is a more preferred adsorbate [6]. Most metal-organic frameworks (MOF) exhibit *S*-type water adsorption isotherms which can provide a better water exchangeable volume [7]. Ehrenmann *et al.* [8] found that the adsorption capacity of MIL-101(Cr) per gram of water vapor showed stability in multiple cycles and is stable even over several cycles, MIL-101(Cr) may be the most promising adsorbent material of adsorption chillers.

Benjamin *et al*. [9] prepared the alkali doped MIL-101(Cr) material and the structural properties are evaluated by scanning electron micrography, X-ray diffraction, thermo-gravimetric analyser and N_2 adsorption analysis. Found that the surface characteristics of alkali (Li^+, Na^+, K^+) doped MIL-101(Cr) metal organic frameworks increase the water uptakes at lower relative pressure region with fast kinetics. This MOF can be used as potential adsorbents for various low temperature heat transmission applications. Rui *et al*. [10] synthesized MIL-101(Cr) by hydrothermal method and the powder prepared was pressed into a desired shape and the adsorption refrigeration performance of shaped MIL-101(Cr)-water working pair was studied on the simulation device of adsorption refrigeration cycle system. Found that when the evaporation temperature is 10 °C and the molding pressure is 3 MPa, the cooling capacity of MIL-101(Cr)-water is 2.24 times than that of the silica gel-water working pair. The MIL-101(Cr)-water working fluid pair has excellent adsorption refrigeration performance. Elsayed *et al.* [11] added $CaCl_2$ to the MIL-101 (Cr) structure to significantly enhance the water adsorption characteristics within the desired relative pressure range. Liu *et al.* [12] prepared MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20%, MIL-101(Cr)/$CaCl_2$-30% composites by immersion method and found that the specific surface area, total pore volume and pore size distribution of micropores and mesopores of MIL-101(Cr)/$CaCl_2$ composites decreased with the increase of $CaCl_2$ content. The $CaCl_2$ composite with a mass fraction of 30% agglomerates seriously after absorbing water. The MIL-101(Cr)/$CaCl_2$-20% exhibited superior water vapor adsorption performance and have great potential for application adsorption heat pumps. Liu *et al*. [13] synthesized MIL-101(Cr)/$CaCl_2$ composites with $CaCl_2$ mass fractions of 10% and 20%, and verified the adsorption performance of the material at different temperatures through simulations and experiments, the results showed that the levels of COP and specific cooling power (SCP) decreased with the increase in the adsorption temperature.

Hamid and Iman *et al*. [14] presented a numerical model of combined heat and mass transfer in the adsorbent bed of a silica gel-water adsorption chiller for a cylindrical bed with annular fins. Gamze *et al.* [15] analyzed the effect of adding metal additives to the adsorption bed on the performance of adsorption coolers. The material, shape and the location of the heating/cooling fluid pipe, as well as the adsorbent particle radius, are predicted, and their influence on the specific cooling performance of the adsorption chiller is analyzed. The obtained results showed that the adsorbent particle radius change and the distance between the fins have important roles in SCP. The effect of aluminum particle additive on SCP of the adsorption heat pump is observed as 300% of increment. Saleh *et al*. [16] experimentally and numerically investigates the performance of a wire finned heat exchanger compared to rectangular finned and micro-channel heat exchangers. The performance of the wire finned heat exchanger packed with aluminum fumarate was investigated in terms of water uptake and surface temperature at various fin height (3.5 mm, 7 mm, and 14 mm), spacing (1 mm, 2 mm, and 3.5 mm) and tube diameter (6 mm, 9 m, and 12 mm). Sharafian *et al*. [17] divided the adsorption bed into nine types and they found that the finned tube adsorption bed design has better performance, and pointed out that the fin spacing and height of the adsorption bed should be optimized to improve the thermal conductivity of adsorbent material. Liu *et al*. [18] used the large temperature jump method to carry out the dynamic adsorption and desorption experiments of three kinds of adsorbents at variable temperature and constant pressure. The dynamic adsorption and desorption model is established and combined with the experimental results to calibrate and verify the combination of heat and mass transfer coefficients of adsorbents. The results showed the addition of calcium chloride increases the range of suitable cooling conditions for MIL-101(Cr), when the desorption temperature is 90 °C, the minimum evaporation temperatures of MIL-101 (Cr) and MIL-101 (Cr)/$CaCl_2$-20% are 12 °C and 5 °C, and the maximum adsorption temperatures are 31 °C and 38 °C, respectively. Baiju *et al*. [19] considered the adsorbent mass is 45 kg with a shifting duration of 20 seconds, the inlet chilled water temperature in the evaporator, temperature of cooling water and hot water temperature of the adsorbent bed and its effect on systems coefficient of performance, refrigeration effect and specific cooling power have been studied and presented.

According to the literature review, as for MOF, the preparation period for preparing a large number of materials is relatively long. Although the performance of the material in the experimental bench can be verified, the vacuum maintenance effect of the experimental bench itself and the pipe resistance affect the real performance evaluation of the material. Through simulation modelling, the application effect of new MOF in adsorption refrigeration can be demonstrated to a greater extent. Through the optimization of the fin bed structure, the optimal fin bed structure of different composite materials can be simulated to better help select and application materials. The MIL-101(Cr) may be the most promising adsorbent material of adsorption chillers, and the addition of $CaCl_2$ increases the range of suitable cooling conditions for MIL-101(Cr). The composite material of MIL-101(Cr)/$CaCl_2$ show excellent adsorption performance and application potential of adsorption refrigeration, but the influence of adsorption bed structure on MIL101 (Cr) pure materials and composites has not been demonstrated.

In order to better show the performance of this new MOF at the initial stage of their application and screening, this paper uses the openmodelica simulation platform to develop a customized solver and solution method to simulate the single-bed finned tube adsorption refrigeration system model of MIL-101(Cr) composite-water adsorption chillers, since the $CaCl_2$ composite with a mass fraction of 30% agglomerates seriously after absorbing water, only comparing the adsorption refrigeration performance of MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20%. The finned tube adsorption bed is specifically optimized, and the refrigeration performance of the material under different fin thickness/length/number is obtained, and the optimal adsorption bed structure is obtained for different materials.

System modelling and description

Adsorption refrigeration system model library based on modelica language

Circulating water inlet/outlet model

This paper uses the WaterIF97-pT library to calculate thermal properties of water and water vapor. The transfer and calculation of thermodynamic properties of water and steam are focused in this model.

Compile codes through modelica language to realize calculation function of thermodynamic property parameters of water in two saturated states of liquid and gas. The media model is introduced into circulating water inlet model for physical property calculation, and water inlet temperature, flow rate, and pipe diameter parameters are set. After aforementioned parameters are input, inlet water flow rate and inlet water enthalpy value are obtained. The default parameters of inlet flow rate are 0.1 m/s, inlet temperature is 303 K, and pipe inner diameter is 0.01 m.

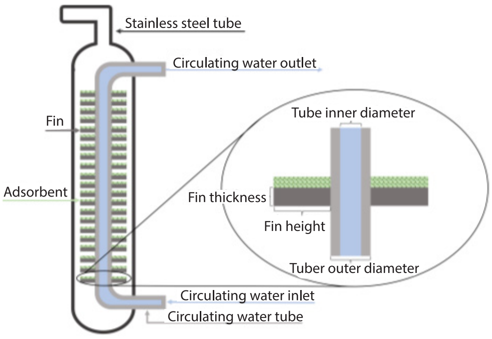

Figure 1. Schematic diagram of physical structure of adsorption bed

Heat exchanger pipe model

The adsorption bed is the core of adsorption refrigeration system and finned tube adsorption bed structure is the most common. The physical structure of adsorption bed is shown in fig. 1.

For the establishment of heat exchange pipe model, heat exchange pipe is firstly discretized, the research object is divided into multiple equal control volumes by finite volume method, and then a finite volume model is established for each control volume. It can be seen from the overall structure of the adsorption bed, the main functions of the heat exchange pipes and the materials of the pipes that the heat exchange between the pipes and the surrounding environment is far less than that between the pipes and fins. At the same time, the heat exchange pipe is short and has no complex structure, the fluid in the pipe is fully developed, the fluid pressure drop can be ignored. The heat transfer between the circulating working medium and the pipe, and between the pipe and the fin are the main objects to be considered in the heat exchange pipe model.

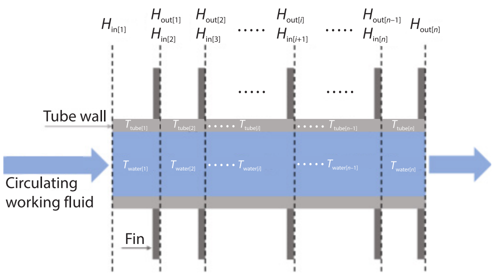

Figure 2. Schematic diagram of discretization model of heat exchange pipe

The discretization model of heat exchange pipes is shown in fig. 2. The entire heat exchange pipe is discrete according to the number of fins, and each heat exchange unit includes fins, pipes and working fluid.

Energy conservation equation of circulating working fluid:

$$\frac{\partial H_i}{\partial x} = hS_i\left(T_{\text{water},i} - T_{\text{tube},i}\right) \tag{1}$$

$$H_{\text{out},i} = \dot{m}C_pT_{\text{water},i} \tag{2}$$

$$H_{\text{out},i} = H_{\text{in},i+1} \tag{3}$$

Heat transfer coefficient between working fluid and pipe-line, h, calculated by the Dittus-Boelter equation:

$$\text{Nu}_f = 0.023\text{Re}_f^{0.8}\text{Pr}_f^n \tag{4}$$

$$\text{Nu}_f = \frac{hd}{\lambda} \tag{5}$$

$$\text{Re}_f = \frac{ud}{\nu} \tag{6}$$

$$\mathrm{Pr}_f = \frac{C_p \nu}{\lambda} \tag{7}$$

The energy conservation equation of the tube wall:

$$C_\mathrm{w} \pi \left[\left(\frac{d_\mathrm{out}}{2} \right)^2 - \left(\frac{d_\mathrm{in}}{2} \right)^2 \right] \frac{L}{n} \rho_\mathrm{cu} \frac{\mathrm{d}T_{\mathrm{pipe},i}}{\mathrm{d}t} = Q_{\mathrm{wf},i} + Q_{\mathrm{flow},i} \tag{8}$$

The thermal interface in heat exchange unit is used to connect heat exchange tube and fin, including heat conduction of fin and heat exchange between fin and adsorbent. The model contains same number of interfaces as the number of discrete units.

Finned bed model

The finite volume method is used to solve dispersion of fins. The solution is decomposed into n sections, and the differential equations solved by each control body are integrated to obtain a discrete equation set. Meanwhile, each decomposed control body is inserted into heat exchange interface as a heat exchange interface with adsorbent. The adsorption bed is continuously heated/cooled by the heat exchange pipe, with strong heat exchange capacity, which is much higher than the heat exchange with the surrounding environment. With adsorbent adsorption and desorption as the main research object, the heat exchange between fins and the surrounding environment can be ignored. The fin bed model mainly considers the transverse heat conduction of fins and the heat transfer between fins and adsorbent.

The fin bed model is shown in fig. 3, where subscript i represents the number of fins and j represents the number of discrete points. Each heat exchange unit in the discrete fin bed model includes two parts of heat exchange, one is the heat transfer of the fins, and the other is heat exchange between fins and adsorbent.

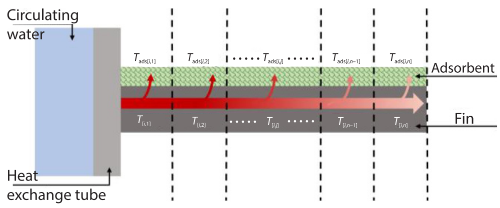

Figure 3. Schematic diagram of discretization model of fin bed

The energy conservation equation of the heat exchange unit:

$$m_{i,j} C_\mathrm{Al} = -h_\mathrm{fa} A_{\mathrm{fa}_{i,j}} \left(T_{i,j} - T_{\mathrm{ads}_{i,j}} \right) - k A_{\mathrm{ff}_{i,j}} \left(T_{i,j} - T_{i,j-1} \right) - k A_{\mathrm{ff}_{i,j}} \left(T_{i,j} - T_{i,j+1} \right) \tag{9}$$

$$m_{i,j} = \rho_\mathrm{Al} \pi \left(r_{\mathrm{fin}_{j+1}}{}^2 - r_{\mathrm{fin}_j}{}^2 \right) d_\mathrm{fin} \tag{10}$$

$$r_{\mathrm{fin}_{j+1}} = r_{\mathrm{fin}_j} + \Delta x \tag{11}$$

$$\Delta x = \frac{X_0}{n_\mathrm{dis}} \tag{12}$$

$$A_{\mathrm{fa}_{i,j}} = \pi \left(r_{\mathrm{fin}_{j+1}}{}^2 - r_{\mathrm{fin}_j}{}^2 \right) \tag{13}$$

$$A_{\mathrm{ff}_{\mathrm{i,j}}} = 2\pi r_{\mathrm{fin}_{j+1}} d_\mathrm{fin} \tag{14}$$

Since heat exchange of discrete heat exchange unit at the end only includes heat transfer and heat exchange with adsorbent, and ignores the heat exchange with the surrounding environment, the energy conservation equation:

$$m_{i,n}C_{\mathrm{Al}}\frac{\mathrm{d}T_{i,n}}{\mathrm{d}t}=-h_{\mathrm{fa}}A_{\mathrm{fa}_{i,n}}\left(T_{i,n}-T_{\mathrm{ad}_{i,n}}\right)-kA_{\mathrm{ff}_{i,n}}\left(T_{i,n}-T_{i,n-1}\right) \tag{15}$$

Adsorbents and mass transfer models

In order to facilitate the setting of parameters in the heat and mass transfer of adsorbent and increase the reusability of the model, modelling will be divided into two parts, one is adsorbent model, and the other is the mass transfer model between adsorbent and evaporator/condenser. Adsorbent and mass transfer model established in this section is a discrete model, and energy conservation equation of discrete adsorbent unit:

$$\left(m_{\mathrm{sor}_{i,j}}C_{\mathrm{sor}}+m_{\mathrm{sor}_{i,j}}w_{i,j}C_p\right)\frac{\mathrm{d}T_{\mathrm{ad}}}{\mathrm{d}t}+\dot{m}_{\mathrm{vapor}_{i,j}}u_{\mathrm{ad}_{i,j}}=-h_{\mathrm{fa}}A_{\mathrm{fa}_{i,j}}\left(T_{\mathrm{ad},i,n}-T_{i,n}\right)+\dot{m}_{\mathrm{vapor}_{i,j}}h_{\mathrm{vapor}} \tag{16}$$

$$m_{\mathrm{sor}_{i,j}}=2\pi r_{\mathrm{fin},j}\Delta x d_{\mathrm{ad}}\rho_{\mathrm{ad}} \tag{17}$$

Adsorbent model and the mass transfer model are connected through a flow interface. The instantaneous adsorption capacity and internal energy of adsorption phase in eq. (16) are calculated by mass transfer model, this model should also be combined with the characteristic curve fitting equation of MIL-101(Cr) composite material to obtain a mass transfer model corresponding to each material:

$$\dot{m}_{\mathrm{vapor}_{i,j}}=\beta\left[W\left(A\right)_{i,j}-w_{i,j}\right] \tag{18}$$

$$A_{i,j}=\mathrm{R}T_{\mathrm{ad}i,j}\ln\frac{P_{\mathrm{sat}}\left(T_{\mathrm{ad}}\right)_{i,j}}{P_{\mathrm{ad}_{i,j}}} \tag{19}$$

$$u_{\mathrm{ad}_{i,j}}=h_{\mathrm{ad}_{i,j}}-\frac{P_{\mathrm{ad}_{i,j}}}{\rho_l\left(T_{\mathrm{ad}_{i,j}}\right)} \tag{20}$$

$$h_{\mathrm{ad}_{i,j}}=\Delta h_{\mathrm{ad}_{i,j}}+h_{\mathrm{vapor}_{i,j}} \tag{21}$$

$$\Delta h_{\mathrm{ad}_{i,j}}=-\Delta h_{\mathrm{v}_{i,j}}-A_{i,j}+T_{\mathrm{ad}_{i,j}}\alpha_{i,j}\left(\frac{\partial A_{i,j}}{\partial\ln W_{i,j}}\right)_{T_{\mathrm{ad}_{i,j}}} \tag{22}$$

$$\alpha_{i,j}=-1/\rho_l\left(T_{\mathrm{ad}_{i,j}}\right)\frac{\partial\rho_l\left(T_{\mathrm{ad}_{i,j}}\right)}{\partial T_{\mathrm{ad}_{i,j}}} \tag{23}$$

Evaporator/condenser model

In the evaporator/condenser model, set adsorption and desorption temperature in the system, and obtain saturated water vapor pressure at a certain temperature, use flow interface to connect with the mass transfer model, and transfer pressure variable to the mass transfer model to complete Calculation of adsorption and desorption process.

Performance evaluation index

After establishing a complete system model, it is necessary to establish a system performance evaluation index function. In this paper, COP and SCP are used as system evaluation index functions which can reflect the advantages and disadvantages of the heat transfer performance of the adsorption bed. The calculation formulas are:

$$COP = \frac{Q_e}{Q_h} \tag{24}$$

$$SCP = \frac{Q_e}{t_{\text{cycle}} m_{\text{sor}}} \tag{25}$$

$$Q_e = \int_{t_{\text{ads}_{\text{start}}}}^{t_{\text{ads}_{\text{end}}}} L_{\text{g}} \dot{m}_{\text{vapor}} \text{d}t \tag{26}$$

$$Q_h = \int_{t_{\text{des}_{\text{start}}}}^{t_{\text{des}_{\text{end}}}} H_{\text{in}} - H_{\text{out}} \text{d}t \tag{27}$$

Single-bed fin-tube adsorption refrigeration system model

Simulation models of each component of single-bed fin-tube adsorption refrigeration system were established, connect and integrate these component models to obtain a complete system model, as shown in fig. 4.

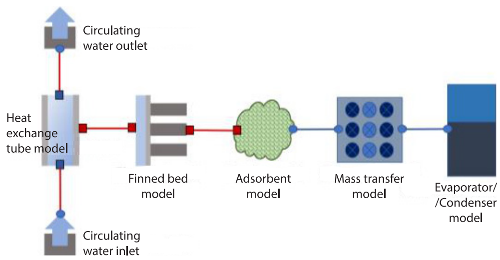

Figure 4. Single bed finned tube adsorption refrigeration system model diagram

In order to validate the accuracy of the model, this paper compares with the experimental data of Ellis [20]. The experimental device used active carbon/ammonia as the working pair, the adsorption bed began to cool at 418 K, and the temperature change of the adsorption bed was recorded for ten minutes. Additional data for the experiment can be found in its article. Figure 5 shows the time change of the fluid leaving the bed temperature in the experimental device and the comparison of the numerical simulation. The numerical simulation is agreement with the experimental data.

As the change of outlet temperature is directly related to the adsorption and desorption behavior in the bed during the adsorption cycle. The agreement between the results is important and an indication of the proper mathematical modelling and the accuracy of the numerical scheme.

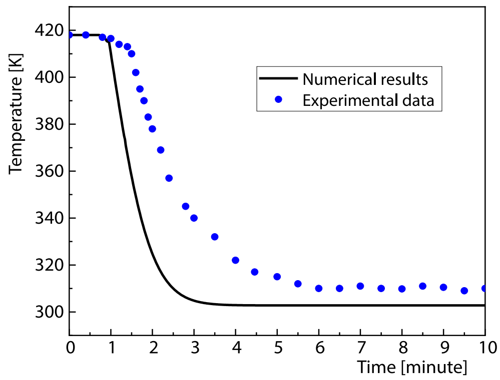

Figure 5. Comparison of experimental and simulated values of heat flow temperature with time

Preparation and property determination of materials

Preparation of materials

Based on previous studies, MIL-101(Cr) may be the most promising adsorbent material of adsorption chillers, and the addition of $CaCl_2$ increases the range of suitable cooling conditions for MIL-101(Cr). The composite material of MIL-101(Cr)/$CaCl_2$ show excellent adsorption performance and application potential of adsorption refrigeration. The $CaCl_2$ composite with a mass fraction of 30% agglomerates seriously after absorbing water. MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10%, and MIL-101(Cr)/$CaCl_2$-20% was used for this research.

Here, MIL-101(Cr) is prepared by hydrothermal synthesis method and the synthesis of MIL-101(Cr) composite material is prepared by impregnation method with 10% and 20% $CaCl_2$. Since the specific surface area, total pore volume and pore size distribution of micropores and mesopores of MIL-101(Cr)/$CaCl_2$ composites decreased with the increase of $CaCl_2$ content. After synthesis, XDR physical property analysis verified that MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10%, and MIL-101(Cr)/$CaCl_2$-20% were successfully prepared. The specific synthesis process and performance characterization of materials are shown in another paper of our research group [12].

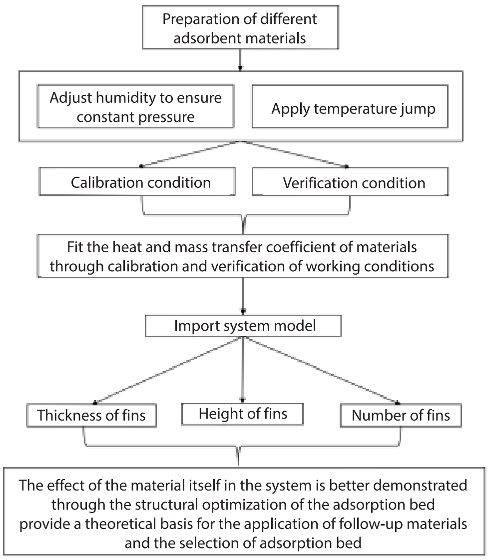

Figure 6. Diagram of experimental method and purpose

Performance of materials

In order to explore adsorption performance of MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10%, and MIL-101(Cr)/$CaCl_2$-20%, use a dynamic water vapor adsorption instrument to achieve continuous cooling of the material. The experimental method and purpose are shown on fig. 6.

Experimental method is the large temperature jump method, which used to induce the adsorption process by applying a temperature jump to a small amount of material sample under a preset pressure. With the change of material temperature, maintain constant pressure by changing the humidity around the material, simulates adsorption and desorption process of the material under variable temperature and constant pressure. Set up two sets of working conditions to verify the performance of the material. Specific working conditions are shown in tab. 1. As the temperature rise process is slower than the temperature drop process, in the actual temperature rise desorption process, taking the complete desorption process will lead to large errors in the subsequent model calibration, so the desorption here only takes the part where the temperature rises from 55-60 °C, which does not represent the complete desorption capacity of the material. Working condition one is calibration group, the other is validation group. The pressure during adsorption process under two working conditions is maintained at 1.23 kPa (at 10°C, saturated water vapor pressure). The adsorption and desorption experiment results of three materials under two working conditions are shown in tab. 2.

Table 1. Condition setting of adsorption and desorption experiment

Condition	Cooling adsorption			Heating desorption		
	Evaporation temperature	Adsorption temperature	Desorption temperature	Initial temperature	End temperature	Relative humidity
One	10 °C	30 °C	75 °C	55 °C	60 °C	26.9%
Two	10 °C	30 °C	70 °C	60 °C	65 °C	21.3%

Table 2. The adsorption and desorption of three materials under two working conditions

Adsorbent	Working condition one			Working condition two		
	Equilibrium adsorption capacity [g/g]	Desorption amount [g/g]	Adsorption time [minute]	Equilibrium adsorption capacity [g/g]	Desorption amount [g/g]	Adsorption time [minute]
MIL-101(Cr)	0.111	0.036	150	0.103	0.014	150
MIL-101(Cr)/$CaCl_2$-10%	0.340	0.018	200	0.250	0.050	210
MIL-101(Cr)/$CaCl_2$-20%	0.334	0.054	200	0.332	0.074	200

In the experimental results, it only took 34 minutes for MIL-101(Cr)/$CaCl_2$-10% to reach the equilibrium adsorption capacity of MIL-101(Cr)(0.111g/g), and 32 minutes MIL-101(Cr)/$CaCl_2$-20% to reach the equilibrium adsorption capacity of MIL-101(Cr)(0.111g/g). The addition of $CaCl_2$ is beneficial for the material to achieve better water adsorption performance. Finally, the equilibrium adsorption capacity of MIL-101(Cr)/$CaCl_2$-10% is 0.340g/g, and 0.334g/g for MIL-101(Cr)/$CaCl_2$-20%. As a hygroscopic salt, calcium chloride greatly improves the adsorption capacity of MIL-101(Cr), it can be seen that the equilibrium adsorption capacity of MIL-101(Cr)/CaCl2-10% improved 206% than pure MIL-101(Cr), and MIL-101(Cr)/$CaCl_2$-20% improved 201% than pure MIL-101(Cr). The equilibrium adsorption capacity of MIL-101(Cr)/$CaCl_2$-20% is slightly lower than MIL-101(Cr)/CaCl2-10%, When the mass fraction of calcium chloride is 20%, part of the pore diameter of MIL-101(Cr) is blocked, which slightly affects the adsorption capacity.

Then, combination of calibration working condition and verification working condition, the least squares method of measured and simulated loads is used to fit heat transfer coefficient, α, and mass transfer coefficient, β. For a given set of α and β, the root means square error (RMSE) between measured and simulated loads:

$$RMSE = \sqrt{\frac{\int_0^\tau \left(w_{\text{meas}} - w_{\text{sim}}\right)^2 \text{d}t}{\tau}} \tag{28}$$

In order to better compare different experiments, RMSE is normalized with measured average load to obtain the coefficient of variation (CV):

$$CV\left(RMSE\right) = \frac{RMSE}{\int_0^\tau w_{\text{meas}} \frac{\text{d}t}{\tau}} \tag{29}$$

According to the aforementioned method, CV values of the experimental and simulation results of adsorption and desorption process of three different materials under working conditions are obtained, and suitable heat and mass transfer coefficient combinations are selected for different materials in different processes, as shown in tab. 3.

The mass transfer and heat transfer coefficients of each material are brought into model to verify the difference between actual adsorption amount change and simulation of working Condition 2. According to the simulation results, difference between two working conditions is within 5%, therefore, the material performance parameters under working Condition 1 can be further used. And it can be seen that after adding $CaCl_2$, heat transfer coefficient of the material decreases.

Table 3. The combination of heat transfer coefficients determined in the calibration model

	α [Wm^{-2}K^{-1}]	β [kgs^{-1}]	CV [%]
MIL-101(Cr)-adsorption	40	$1 \cdot 10^{-5}$	4.6
MIL-101(Cr)-desorption	100	$4 \cdot 10^{-7}$	4.4
MIL-101(Cr)/$CaCl_2$-10%-adsorption	16	$2 \cdot 10^{-5}$	3.5
MIL-101(Cr)/$CaCl_2$-10%-desorption	60	$8 \cdot 10^{-7}$	1.1
MIL-101(Cr)/$CaCl_2$-20%-adsorption	20	$2 \cdot 10^{-5}$	2.5
MIL-101(Cr)/$CaCl_2$-20%-desorption	40	$2 \cdot 10^{-7}$	2.3

The heat and mass transfer coefficients obtained previously are used as the parameters of the dynamic adsorption model to obtain suitable values of MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20% range of refrigeration conditions. This process ignores energy dissipation in heat exchanger that transfers heat to adsorbent bed, heat exchange loss at evaporator end, and the adsorption and desorption time, and determine COP value of the material. Calculate the COP of the material under conditions of desorption temperature of 90 °C, evaporation temperature of 5-18 °C and adsorption temperature of 25-38 °C. The specific process of model calibration and verification was in another paper of our research group [18].

Table 4. The COP value of three materials

	Value of COP		Evaporation temperature [°C]	Adsorption temperature [°C]
MIL-101(Cr)	Maximun	0.708	18	25
	Minimum	0.022	5	38
MIL-101(Cr)/$CaCl_2$-10%	Maximum	0.710	18	25
	Minimum	0.074	5	38
MIL-101(Cr)/$CaCl_2$-20%	Maximum	0.64	18	25
	Minimum	0.216	5	38

The COP of three different materials increases with the increase of evaporation temperature and decrease of adsorption temperature. The COP can reach about 0.7 within the scope of refrigeration conditions, tab. 4. The MIL-101(Cr) can adapt to an increased range of refrigeration condition with the addition of $CaCl_2$, when MIL-101(Cr), MIL-101(Cr)/ $CaCl_2$-10%, and MIL-101(Cr)/$CaCl_2$-20% at evaporation temperature of 5 °C and adsorption temperature of 25 °C, COP values are 0.107, 0.233, and 0.400, respectively.

Results and discussion

Analysis of the number of discrete units in a single-bed fin-tube adsorption refrigeration system model

The number of fins is 30, height of the fins is 30 mm, thickness of the fins is 0.5 mm, and the evaporation temperature is 10 °C, condensation temperature is 30 °C, and desorption temperature is 90 °C, calculate the COP and SCP of MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20% under this condition, respectively, where the fin bed number of discrete units of the model is 20, 40, 80, 160, 320, and the calculation results are shown in fig. 7.

The aforementioned results show that as the number of discrete units increases, the response speed of heat and mass transfer of each discrete unit of adsorbent material is accelerated.

Therefore, COP and SCP of adsorption refrigeration system filled with three different adsorbents first increase and then gradually increase. When the number of discrete units is 160, the change of system COP/SCP tends to be gentle. The number of discrete units of bed model is 160.

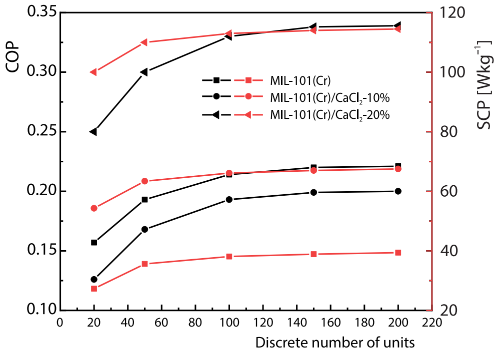

Figure 7. The variation law of system COP/SCP with the number of discrete units

The influence of the number, height and thickness of fins on the properties of three materials

Analysis of the influence of the number of fins and the thickness of the fins on the performance of the system

Through numerical simulation of adsorption system performance of MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20% under different fin numbers and fin thicknesses, obtained the change rule of adsorption bed performance with two factors. The height of fins is 20 mm, the number of fins is 10, 20, 30, 40, 50, the thickness of fins is 0.3 mm, 0.4 mm, 0.5 mm, 0.6 mm, 0.7 mm, and the cycle period is set to 2000 seconds, in which adsorption and desorption Each time is 1000 seconds.

It can be seen from figs. 8-10 that the number/thickness of fins have same effect on adsorption refrigeration system using three different adsorbents. The COP decreases with the increase of fin thickness, and the fin number of slices has little effect on COP. On the one hand, because the increase in thickness of fins does not increase the quality of adsorbent, the adsorption capacity does not change, but more heat needs to be supplied to adsorbent bed, so as the thickness increases, system COP tends to decrease. On the other hand, when the thickness of fin is constant, increase in the number of fins is equivalent to increasing the quality of adsorbent, adsorption capacity has increased, and heat transfer of adsorbent bed is increased, but COP is determined by two factors, the cooling capacity and heat exchange amount, so the number of fins has little effect on COP of the system. As for SCP, when it's under the same fin thickness, SCP of the system decreases as the number of fins increases. As the number of fins increases, heat transfer time for each fin to reach a steady-state is prolonged. Meanwhile, the increase in the number of fins leads to an increase in the quality of adsorbent. As heat transfer efficiency of fins decreases, adsorption performance of adsorbent becomes worse. The more fins, the lower system SCP is. The results also show that although increasing the thickness of fins can increase system SCP when the number of fins is small, the change of SCP is small, the maximum amplitude is 1 W/kg. Therefore, increasing the fin thickness cannot effectively improve the SCP of system. From the perspective of economics of adsorbent bed, it may be an unreasonable method.

In order to compare the performance of three materials in the system, the number of fins is taken as 30, COP and SCP of the system change with the thickness of fins, as shown in fig. 1. The results showed that the addition of $CaCl_2$ increased adsorption capacity of the composite material under this working condition. The adsorption capacity increased significantly, and the system COP increased. The MIL-101(Cr) /$CaCl_2$-20% has the largest COP with a value of 0.361. The average SCP of MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20% is 20 W/kg, 44 W/kg, and 74 W/kg, respectively. it means that adding a small amount of $CaCl_2$ increases the adsorption capacity of original MIL-101(Cr) under this working condition. Since increasing the thickness of fins does not increase the quality of adsorbent and cooling capacity of the system, it has almost no effect on SCP of the system.

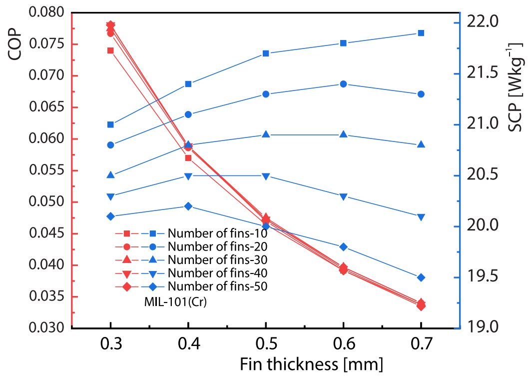

Figure 8. The relationship between the COP/SCP of the system with MIL-101(Cr) as adsorbent varies with the number and thickness of fins

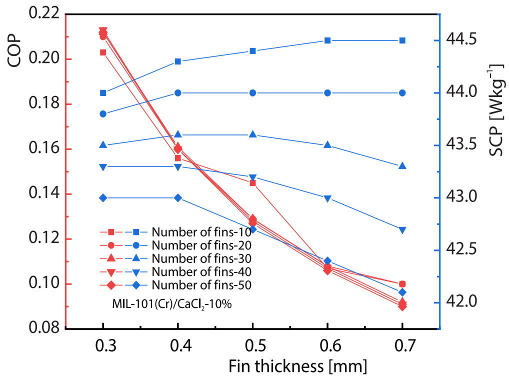

Figure 9. The relationship between the COP/SCP of the system with MIL-101(Cr)/CaCl$_2$-10% as adsorbent varies with the number and thickness of the fins

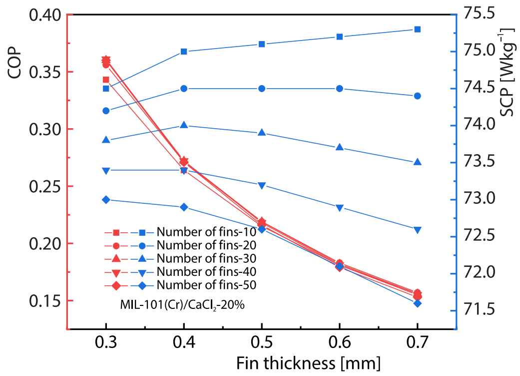

Figure 10. The relationship between the COP/SCP of the system with MIL-101(Cr)/CaCl$_2$-20% as adsorbent varies with the number and thickness of the fins

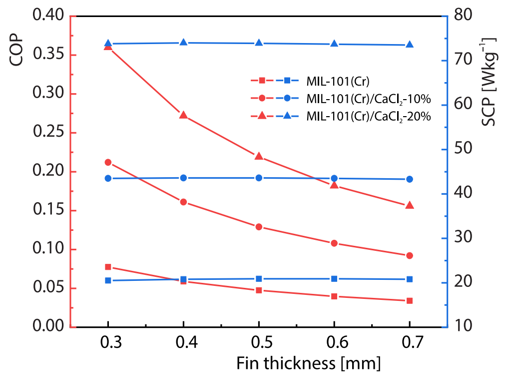

Figure 11. The relationship between the COP/SCP of the system with MIL-101(Cr) and composite materials as adsorbent varies with the thickness of the fins

Analysis of the influence of the number of fins and the height of the fins on the performance of the system

Through numerical simulation of the adsorption system performance of three materials under different fin numbers and fin heights, it is concluded that adsorption bed performance varies with two factors. The number of fins is 10, 20, 30, 40, 50, and the thickness of fins is 0.5 mm. The fin height of adsorption refrigeration system using MIL-101(Cr) as adsorbent is 20 mm, 30 mm, 40 mm, 50 mm, 60 mm, the fin height of the system using MIL-101(Cr) composite material as adsorbent is 20 mm, 30 mm, 40 mm, 50 mm, 60 mm, 70 mm, 80 mm, and cycle period is 2000 seconds.

The COP/SCP of three materials varies with the number and height of fins as shown in figs. 12-14. At the same fin height, the number of fins has a small effect on COP. When the number of fins is 30, three materials get the largest COP value, and the height of fins of MIL-101(Cr), MIL-101(Cr)/CaCl$_2$-10%, MIL-101(Cr)/CaCl$_2$-20% is 50 mm, 60 mm, and 70 mm, respectively, the system largest COP value of them is 0.065, 0.262, and 0.507, respectively. When the number of fins is constant, as the height of the fins increases, COP of the system first increases and then decreases. This is because the height of fins increases, adsorbent filling volume of the system increases, and the cooling capacity of the system increases. At the same time, it is necessary to provide more heat to the metal layer of adsorption bed, so the height of fins also has an upper limit.

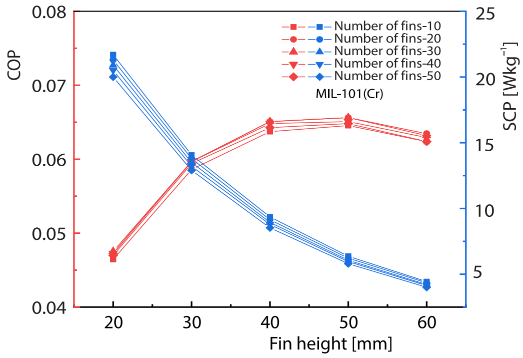

Figure 12. The relationship between the COP/SCP of the system with MIL-101(Cr) as adsorbent varies with the number and height of fins

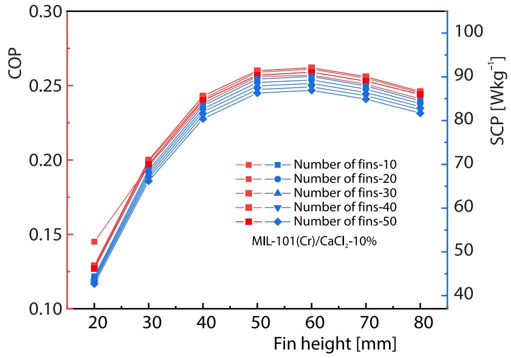

Figure 13. The relationship between the COP/SCP of the system with MIL-101(Cr)/$CaCl_2$-10% as adsorbent varies with the number and height of the fins

With the same fin height, as the number of fins increases, SCP of the system with three materials as absorbent had a tendency to decrease, but at the same fin height, the range of the impact of the number of fins on SCP of the system is less than 2 W/kg, indicating that in this cycle, the number of fins has little effect on the adsorption performance of these adsorbents.

It can be seen that the height of fins is a key factor affecting SCP of the system. The increase in the height of fins increases the quality of adsorbent, cooling capacity of the system increases, but SCP is determined not only by cooling capacity, but also quality of system adsorbent and cycle period. The increased cooling capacity of the system is smaller than that of the quality of adsorbent, so SCP decreases with the increase of fin height. However, as the height of fins increases, SCP of the system with MIL-101(Cr)/$CaCl_2$-10% and MIL-101(Cr)/$CaCl_2$-20% as adsorbent first increase and then decrease. This indicates that the composite $CaCl_2$ material shows strong adsorption capacity under this working condition, and the increase of the adsorp-

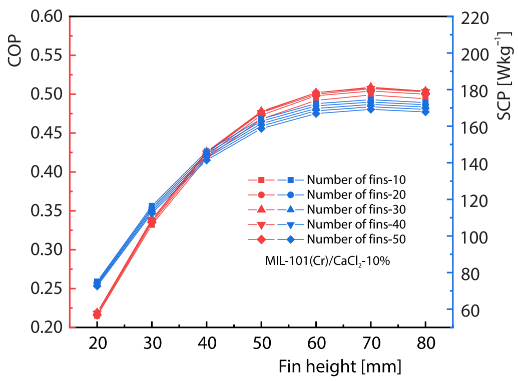

Figure 14. The relationship between the COP/SCP of the system with MIL-101(Cr)/$CaCl_2$-20% as adsorbent changes with the number and height of fins

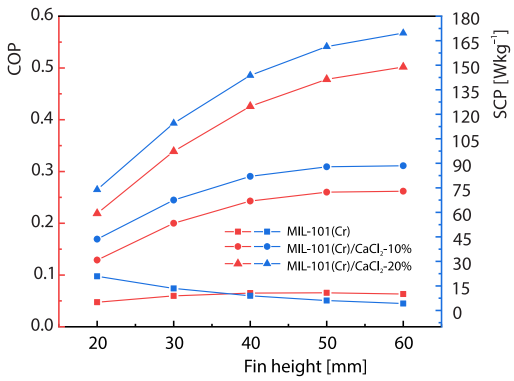

Figure 15. The relationship between the fin height and COP/SCP of the system with MIL-101(Cr) and composite materials as adsorbents

tion capacity caused by the increase of the fin height is obvious. However, the excessive fin height will reduce heat transfer efficiency of the fin and the adsorption capacity of adsorbent, so the fin height still has an upper limit. When the number of fins is 10, they had the largest SCP value, the height of fins of MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20% is 60 mm, 70 mm, respectively, and the largest SCP value of them is 90.1 W/kg, 172.9 W/kg, respectively.

In order to compare the performance of three materials in the system, when the number of fins is 30, the COP and SCP of the system change with the height of fins, as shown in fig. 1. The results show that the addition of $CaCl_2$ increases the adsorption capacity of composite material under this working condition, and COP and SCP values of the system are greatly improved. When the fin height is 60 mm, MIL-101(Cr)/$CaCl_2$-20% COP and SCP are 0.502 and 170 W/kg, respectively.

The effect of adding calcium chloride on the properties of materials in the system

Under the setting conditions three materials all show a trend of COP decreasing with the increase of fin thickness. When the fin thickness of adsorbent bed increases from 0.3 mm to 0.7 mm, COP value of MIL101(Cr), MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20% in the system drops from 0.0701-0.0335, 0.213-0.09, and 0.3612-0.153, respectively. As for fin height, COP of three materials all show a trend of first increasing and then decreasing with the different of fin height which is within 20-80 mm, and COP value of MIL101(Cr), MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20% in the system fluctuates in the range of 0.0465-0.065, 0.127-0.262, and 0.215-0.507, respectively.

It can be found in the system, with the change of the number/height/thickness of fins, the materials after adding $CaCl_2$ all show better performance. When the mass fraction of $CaCl_2$ is 20%, the COP of the system is twice than that of 10% $CaCl_2$, and 4-8 times than that of pure MIL-101(Cr).

Conclusions

In this paper, the combination of heat and mass transfer coefficients of three materials is calibrated and verified through low cost small scale experiments, by combining the adsorption properties of three materials (MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10% and MIL-101(Cr)/$CaCl_2$-20%) with a single-bed finned tube adsorption refrigeration model to verify the effect of different adsorption bed structures on the adsorption performance of the material on the system. The main conclusions are as follows.

- The number of fins has a small impact on the COP and SCP of the system. The impact on the COP is less than 0.03, and the impact on SCP is less than 2 W/kg, indicating that the heat exchange fluid and the heat exchange tube have a relatively high difference and strong heat transfer ability. The increase in the number of fins has a small effect on the heat transfer of each fin, so increasing/decreasing the number of fins is not the best choice to improve the system COP.
- When the number and height of the fins are constant, as the thickness of the fins increases, the heat gain of the fin bed increases, and the COP of the system tends to decrease obviously; the SCP of the system first increases and then decreases, but the impact range is still less than 2 W/kg, and the system cooling capacity changes a little. Therefore, choosing thinner fins when designing fins can improve the COP of the system.
- When the number and thickness of the fins are constant, as the height of the fins increases, take MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20% as adsorbent, the

COP of system shows a trend of increasing first and then decreasing. The MIL-101(Cr), MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20% have the highest COP when the best fin heights are 50 mm, 60 mm, and 70 mm, respectively. Due to the low adsorption capacity of MIL-101(Cr) under simulated conditions, the SCP of the system decreases as the height of the fin increases. When the height of the fin is 20 mm, the maximum SCP is 21.7 W/kg. As for MIL-101(Cr)/$CaCl_2$-10%, MIL-101(Cr)/$CaCl_2$-20%, the SCP increases first and then decreases, when their fin height is 60 mm and 70 mm, respectively, the maximum SCP of the system is 90.1 W/kg, 174.5 W/kg, respectively.

Therefore, the fin height has a greater impact on the performance of the system. When designing the adsorbent bed, the appropriate fin height should be selected for the specific adsorbent.

Acknowledgment

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Nomenclature

A_{fa} – the area of contact with adsorbent of the fins, [m^2]
A_{ff} – contact area between the fins, [m^2]
C_p – constant pressure specific heat of working fluid, [kJkg^{-1}K^{-1}]
C_w – specific heat capacity of copper tube, [kJkg^{-1}K^{-1}]
C_{Al} – fin specific heat capacity, [kJkg^{-1}K^{-1}]
C_{sor} – adsorbent specific heat capacity, [kJkg^{-1}K^{-1}]
d – characteristic length, [m]
d_{in} – inner diameter of tube, [m]
d_{out} – outer diameter of tube, [m]
d_{ad} – adsorbent thickness, [m]
d_{fin} – fin thickness, [m]
H – enthalpy flow of circulating working fluid, [W]
H_{in} – enthalpy flow at the entrance of the heat exchange tube, [W]
H_{out} – heat exchange tube outlet enthalpy flow, [W]
h – heat transfer coefficient between circulating working fluid and pipe-line, [kWm^{-2}K^{-1}]
h_{fa} – heat transfer coefficient between fin and adsorbent, [kWm^{-2}K^{-1}]
h_{vapor} – enthalpy of adsorbate vapor, [kJkg^{-1}]
L – tube length, [m]
L_g – latent heat of vaporization of water, [kJkg^{-1}]
n_{dis} – discrete number of units
Pr_f – Prandtl number
Q_{wf} – Heat exchange between tube wall and fluid working medium, [kJkg^{-1}]
Q_{flow} – Heat flow of thermal interface in heat exchange unit, [kJkg^{-1}]
Re_f – Reynolds number
r_{fin} – inner fin diameter, [m]
m – quality of the heat exchange unit, [kg]
$\dot{m}_{wapor}$ – mass-flow of water vapor, [kgs^{-1}]
m_{sor} – adsorbent quality, [kg]
Nu_f – Nusselt number
n – 0.4 when heating/0.3 when cooling
T – fin temperature, [K]
T_{ads} – adsorbent temperature, [K]
T_{water} – working fluid temperature, [K]
T_{tube} – tube wall temperature, [K]
t_{cycle} – adsorption cycle, [s]
$t_{ads_{start}}$ – start time of adsorption process, [s]
$t_{ads_{end}}$ – end time of adsorption process, [s]
$t_{des_{start}}$ – start time of desorption process, [s]
$t_{des_{end}}$ – end time of desorption process, [s]
u – fluid-flow rate, [ms^{-1}]
u_{ad} – adsorption phase internal energy, [J]
w – adsorption quantity, [kgkg^{-1}]
w_{meas} – dynamic adsorption and desorption experiment adsorption capacity, [kgkg^{-1}]
w_{sim} – dynamic adsorption and desorption model adsorption capacity, [kgkg^{-1}]
X_0 – fin height, [m]
Δx – discrete step

Greek symbols

λ – fluid thermal conductivity, [Wm^{-1}K^{-1}]
ν – fluid kinematic viscosity, [m^{2}s–1]
ρ_{ad} – adsorbent density, [kgm^{-3}]
ρ_{Al} – the density of aluminum, [kgm^{-3}]
ρ_{cu} – copper tube density, [kgm^{-3}]
τ – dynamic adsorption and desorption time, [s]

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