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A THERMOGRAVIMETRIC ANALYZER FOR CONDENSABLE GAS ADSORPTION UNDER SUBATMOSPHERIC CONDITIONS

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We have developed a thermogravimetric system (TG system) for condensable gas adsorption by modifying a standard thermogravimetric analyzer Cahn TG 2121 and performed isotherm measurements of water vapor adsorption on Fuji Davison type RD silica gel and ethanol vapor adsorption on Maxsorp II activated carbon. For the water vapor-silica gel data, our results compare favorably with the data reported by the manufacturer and those obtained from a volumetric method. This confirms the reliability of our TG system for adsorbents which do not swell significantly. In addition, our isotherm data also provide useful design information for the development of adsorption chillers.

Keywords: *activated carbon, adsorption, chiller, isotherm, silica gel, thermogravimetric*

Introduction

Adsorption processes have been prevalently used in gas separation operations and cooling applications. Quantitative evaluations of gas adsorption on adsorbents are crucial to the design and development of adsorption processes. In general the uptake characteristics of adsorbent/adsorbate working pairs can be studied by thermogravimetric, dynamic column breakthrough, and volumetric methods. Most of the current research focuses on non-condensable gas adsorption [1–7] and few reports on condensable gas adsorption. But the latter phenomenon has proven to be an environmentally friendly means to convert waste heat into effective cooling [8–10]. In order to optimize the design of adsorption cooling systems and predict their performance, it is imperative to investigate the adsorption isotherms of such working pairs as water vapor on silica gels, methanol on zeolites and ethanol on activated carbons.

In the broad term of thermogravimetric measurements, Chihara and Suzuki [11] investigated the water vapor adsorption on the type A silica gel by installing a quartz spring balance in a Pyrex glass vessel. The adsorbents were hung from the balance in a glass tube which was immersed in a constant-temperature bath. The Freundlich equation was used to correlate the data for adsorption system simulation. Unfortunately they did not provide the detailed measurement procedure and accuracy of their measurement. Sakoda and Suzuki [12] measured the isotherms for water vapor adsorption on type A silica gel by allowing the adsorbents to achieve equilibrium with an evaporator filled with liquid water and then ascertaining the change of liquid water volume before and after adsorption in the evaporator. The effect of gaseous phase in the system was ignored. The accuracy of such a method can be expected to be significantly compromised as the adsorbed amount is typically very small in comparison to the volume of liquid water. Based on these two studies, Cho and Kim [13] extended the Freundlich correlation for water vapor adsorption on the Fuji Davison type RD silica gel for the performance simulation of an adsorption chiller without providing further experimental details. More recently, Gruszkiewicz *et al.* [14] studied the water adsorption/desorption on microporous solids at elevated temperatures by applying the ORNL isopiestic (thermogravimetric) apparatus.

In terms of the genre of volumetric measuring technique, Chua *et al.* [15] quantified the adsorption isotherms of water vapor on Fuji Davison type RD and type A silica gel by using a constant-volume-variable-pressure system. They found that the Tóth equation can better fit the experimental data for silica gel-water working pair than the Freundlich equation. Halasz *et al.* [16] investigated the adsorption idiosyncrasy of methanol on a hydrophobic Y-zeolite by using the ASDI RXM-100 type instrument. Being a comprehensive and versatile machine capable of measuring over a wide range of conditions, its accuracy cannot unfortunately be as high as a dedicated device fine tuned to the operating conditions as expected of adsorption chillers.

The thermogravimetric method and volumetric technique are at times used independently to verify

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the measurement accuracies. There are also attempts to combine the two approaches into one integral measurement technique. Wang *et al.* [17] compared the experimental data for water vapor adsorption on the Fuji Davison silica gels by using two independent methods (a constant-volume-variable-pressure system and a thermogravimetric method). In that thermogravimetric method, argon gas was used to protect the balance and maintain the pressure. Accuracy was limited as the measured pressure would invariably be an overestimate of the actual vapor partial pressure. Moreover that technique was only applicable and accurate at relatively high temperatures and relatively low vapor pressures. Dreisbach *et al.* [18] used a combined thermogravimetric-volumetric method to measure the isotherm of water vapor/ethanol mixture on activated carbon. The virtue of this method is that it dispenses with the need to employ a gas chromatographic unit or a mass spectrometer for a binary mixture. The system is however elaborated and very expensive.

In the category of the dynamic column breakthrough method, Gubkina *et al.* [19] measured the binary adsorption of methanol and water vapor on activated carbon. This method however employs more modeling assumptions than the thermogravimetric and the volumetric methods and is therefore less direct. On the other hand, it makes use of the largest amount of adsorbent in a single test and is therefore statistically most robust.

Despite the above published works, both theoretical and experimental, there is still a dearth of experimental results and measurement methods that could be commonly used by manufacturers. Most of the above-mentioned thermogravimetric systems are either expensive or inaccurate. For example, a Rubotherm gravimetric analyzer for measuring pure condensable gas adsorption may cost US$150-200k. A normal TG (ca. US$20-50k) cannot be used under pure condensable gas conditions and a carrier gas is typically used to create various partial pressures. In addition, a baffle gas, typically helium, is used to blanket the balance head and ultimately interact with the experimental gas stream. Therefore, the adsorption behavior is investigated under partial pressure conditions that substantially affect the measurement accuracy. While the volumetric method is costed effective and reliable with a sizeable amount of adsorbent, its value is extremely limited with a diminutive amount of adsorbent; this fundamentally stems from the fact that pressure, temperature and volume measurements cannot be as sensitive and precise as mass measurement. In the present work, a reliable thermogravimetric (TG) analyzer (the cost is less than US$70k) is developed for isotherm measurements of condensable gas adsorption on solid adsorbents under pure condensable gas conditions. This system can handle adsorbents at the milligram level and is therefore suitable for advanced materials which are typically available in minute quantity. Its accuracy is firstly verified by using the water vapor adsorption on the Fuji Davison type RD silica gel. The experimental results compared favorably with the literature [15] and manufacturer's data [20]. It is then used to investigate the adsorption isotherms of ethanol on Maxsorp II activated carbons. Those data could provide useful information to the manufacturer for the cost-effective design of adsorption chillers.

Experimental

Figure 1 shows a pictorial view of our purpose built thermogravimetric (TG) analyzer. The schematic of this system is shown in Fig. 2. The system comprises a Cahn TG2121 basic unit, an evaporator immersed in a temperature-controlled bath, a vacuum pumping and pressure regulating subsystem and argon gas supply subsystem. The vapor is generated in an evaporator heated by a constant-temperature bath fitted with a PID controller with a control accuracy of ±0.01°C. The temperature inside the evaporator is measured by a class A RTD temperature sensor with an accuracy of ±0.15°C. The vapor charging flow rate is controlled by a needle valve located immediately after the evaporator outlet. At steady state, the pressure in the measuring chamber can be maintained to within ±0.1 mbar. The adsorbent is placed in the quartz sample bowl inside the reaction chamber of the TG analyzer which has a radiant heater for maintaining a constant temperature. Sufficient thermal insulation is incorporated to reduce heat loss. Changes in the sample mass are measured by the microbalance of the TG analyzer. The temperature inside the reaction cham-

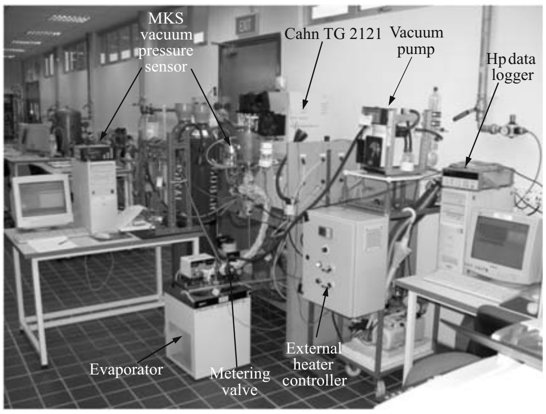

Fig. 1 A pictorial view of our as-built thermogravimetric analyzer

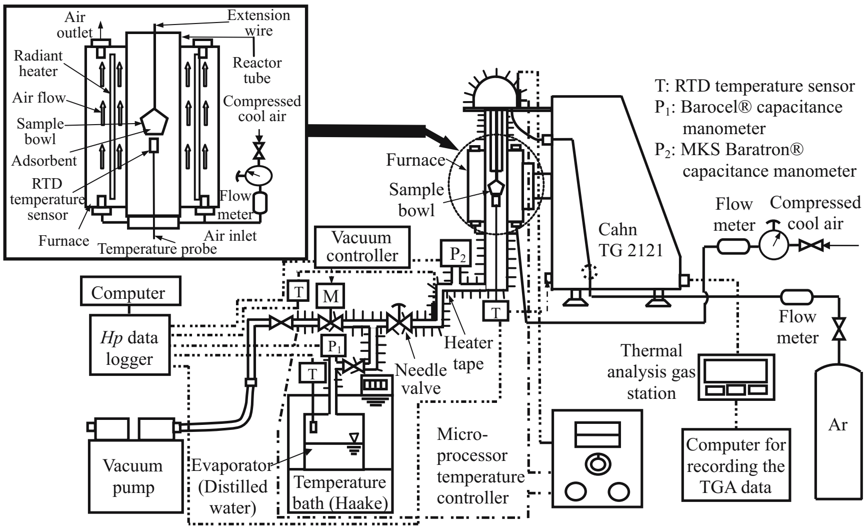

Fig. 2 A schematic of our thermogravimetric analyzer. The inset features of an enlarged sketch of the measuring chamber

ber is monitored by a class A RTD temperature sensor (±0.15°C) which is inserted from the bottom of a tee-joint and the temperature probe tip is positioned exactly under the sample bowl so that the readings can represent the sample temperature at the thermal equilibrium condition. The system pressure is measured with a MKS Baratron® capacitance manometer with an accuracy of ±0.05% of reading mounted at the bottom of the reaction chamber. A vacuum pump is used for vacuuming and purging the system before an experiment and maintaining the chamber pressure in coordination with a vacuum controller. The argon gas, for purging the system, is introduced from the top and within the double walled quartz tubing. Referring to the inset in Fig. 2, the isothermal environment surrounding the silica gel is maintained by direct radiant heating where the heaters are placed outside the hermetic reaction chamber and homogenized by a waft of cooling air through the non-hermetic gap between the reaction quartz chamber and radiant heater. Through a judicious interplay of the heating and cooling effects external to the reaction chamber, a steady temperature environment for the adsorbent can be achieved readily.

The accuracy of the TG balance is firstly verified in vacuo by using a 50 mg and a 100 mg standard mass. We find that the vacuum condition does not affect the balance accuracy and the difference between the reading from the TG balance and the mass of the standard masses is less than 0.1 mg. In order to further investigate the buoyancy effect during the measurements, the standard mass is placed in the sample bowl and measured under the intended experimental conditions. We conclude that the buoyancy effect is negligible after properly controlling the vapor flow rate by adjusting the metering valve. The change in the readings registered by the TG balance of the standard mass during the entire course of verification is less than 0.2 mg. Since the materials which we focus on do not exhibit significant swelling during adsorption, the volume of the adsorbent does not change significantly during the adsorption process. Therefore, our method of using the standard mass could effectively investigate the effects of the buoyant force and the measurement error caused by buoyant force is less than 5%.

In order to avoid vapor condensing along the wall surface of the test system exposed to the environment, the reaction cell and piping system are always kept at least 5–10 K higher than the saturated temperature of the vapor. This is achieved by wrapping heater tapes around the piping system and all parts of the TG analyzer which interact with the environment such as the top cover and quartz tube. The heater tapes are also well insulated to minimize heat loss. Argon gas is not introduced into the system during the actual measurement process for reasons explained later. Hence this arrangement also serves as a very important measure to prevent deleterious condensation on the sensitive measuring device of the gravimetric apparatus.

The dry mass of the adsorbent is firstly measured by using the calibrated moisture balance (Sartorius MA40) in which the adsorbent is maintained at 413 K until there is no further change in mass. The dry mass is once again confirmed inside the reaction chamber of the TG analyzer at 413 K with a continuous purging by argon for about 8 h. At the end of the regeneration process, the whole system is evacuated. Argon as a baffle gas is not introduced during the actual measurement process so that the issues of argon partial pressure, co-adsorption problem and convection problem due to argon are totally eliminated. The reaction cell and evaporator thus form an isolated system. This measurement method also eliminates the diffusion effect caused by concentration difference inside the test system since only the intended vapor is present in the whole test system. The reaction cell is continuously charged with water vapor due to adsorption. The system pressure is maintained by the pre-set pressure in the evaporator and the pressure regulator at the system outlet. Just as in any other measurement devices and methods, absolute thermal equilibrium can hardly be guaranteed. Only technical thermal equilibrium can be achieved during a certain period. We deem the system to have reached thermodynamic equilibrium at a desired pressure and temperature when the mass of the adsorbent and adsorbate remains unchanged (mass fluctuation is less than 0.05 mg) for at least 20 min. This measurement error can be tolerated since the process time of most applications in the air-conditioning and gas separation is less than 60 min. The resultant measurement error is less than 1%. We have also performed experiments where the holding time period is more than 1 h and confirmed that the fluctuations are indeed small. The temperature is measured by a class A RTD sensor for data collection through the TG data recorder and a thermocouple for temperature control. By repeating the above procedures, the uptake capacity of the adsorbent is measured under different temperatures and pressures. For every new test, system checks are performed diligently, namely, (*i*) the system is evacuated, (*ii*) the silica gel is regenerated, and (*iii*) the chamber is purged with the purified inert gas. Uncertainty of the measurements is reduced by repeating the tests at least thrice and a fresh batch of the adsorbents is always used.

Thermodynamics

There are a few types of correlations which are commonly used to describe adsorption isotherms such as the Langmuir equation, Freundlich equation, Radke equation, Tóth equation [21] and t_δ-method [22]. Chua *et al.* [15] found that the Tóth equation could fittingly describe the adsorption experimental data for condensable gas on solid adsorbents, particularly in the saturation region. It is therefore used here to analyze the experimental results and can be described as:

$$q^{*}=K_0\exp\{\Delta_{\mathrm{ads}}H/(RT)\}\cdot$$
$$P/[1+\{K_0/q_{\mathrm{m}}\exp(\Delta_{\mathrm{ads}}H/(RT))\}^{t}]^{1/t}$$

where $q^{*}$is the adsorbed quantity of the vapor phase by adsorbents under thermal equilibrium conditions, q_{m} denotes the adsorption capacity, P, T are the equilibrium pressure and temperature of the system respectively, R is the gas constant, K_0 denotes the pre-exponential constant, and t is the dimensionless Tóth's constant. Tóth observed that the empirical constant t was between zero and one in his experiments, but Valenzuela and Myers [23] reported that t could actually be greater than one. For the Fuji Davison type RD silica gel–water system, it was 12 [15]. $\Delta_{\mathrm{ads}}H$ is the isosteric heat of adsorption and is a key parameter in the design of adsorption chillers. In our data correlating process using the non-linear Tóth equation, we rely on the Van't Hoff equation [21] to help defining the actual parameter space for $\Delta_{\mathrm{ads}}H$.

Results and discussion

We firstly investigate the reliability of our developed thermogravimetric (TG) analyzer. The isotherms of the Fuji Davison silica gel–water systems are known to exhibit zero hysteresis. Hence in the spirit of confirming the reliability of our analyzer, experiments are carried out from low coverage to high coverage (low-high process) and then from high coverage back to low coverage (high-low process). Figure 3 shows two typical measurement procedures for water vapor adsorption on the Fuji Davison type RD silica gel (specific surface area is around 800 m^2 g^{-1}).

Figure 3a presents the temporal uptake curve of water vapor adsorption on the type RD silica gel following the low-high process at 37°C. The adsorption temperature fluctuation is about 0.5°C which is controlled by the PID controller of the Cahn TG2121. The adsorption firstly occurs at a low pressure of 0.66k Pa and water vapor is charged continuously un-

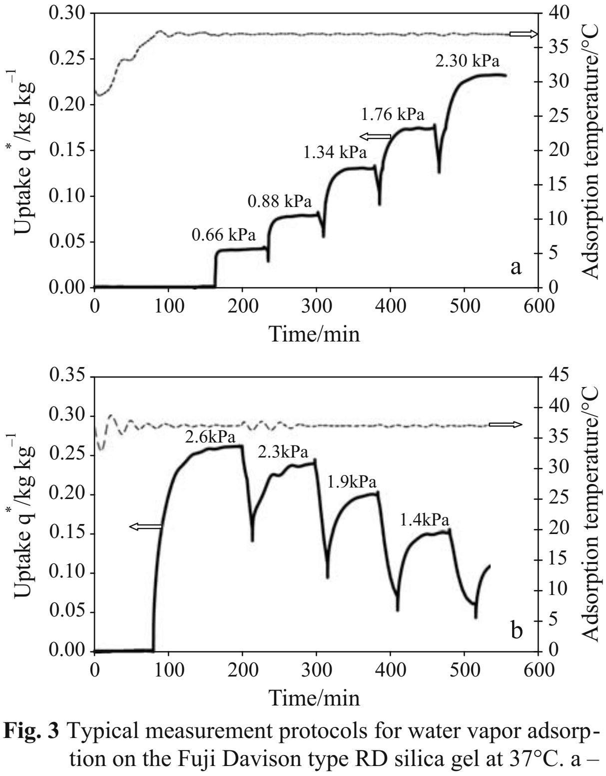

Fig. 3 Typical measurement protocols for water vapor adsorption on the Fuji Davison type RD silica gel at 37°C. a – Progressive adsorption from low to high coverage, b – adsorption from high to low coverage

til the mass change of the adsorbent-adsorbate system inside the sample bowl is less than 0.05 mg within 20 min. The difference of the mass before and after the charging normalized by the dry mass of the adsorbent is the uptake. Once this thermal equilibrium condition is realized at the pre-set pressure and temperature, a new and relatively higher pressure is imposed for the next set of adsorption measurement. Prior to implementing the new set pressure, the system is evacuated followed by vapor charging. By repeating the above procedures, the uptake following the low-high process is obtained at different temperatures and pressures.

Figure 3b features the uptake curve of water vapor adsorption on the type RD silica gel following the high-low process at the preset 37°C. Adsorption equilibrium is firmly established at a relatively high pressure of 2.6 kPa by charging vapor continuously until the mass change of the adsorbent-adsorbate system in the sample bowl is less than 0.05 mg within 20 min. Subsequently the system is evacuated and a new relatively lower pressure of 2.3 kPa is applied. Vapor is introduced into the reaction chamber continuously until a new thermal equilibrium is materialized. The mass change normalized to the original dry mass is the water vapor uptake at this new pressure. By repeating the above procedure, the uptake of water vapor on the type RD silica gel following the high-low adsorption process is obtained at the various pressures and temperatures.

Figure 4 compares the water vapor uptake measurements on the type RD silica gel stemming from the above two processes. It is evident that the difference between these two processes is around 5% which is within the device measurement error. The agreement with known behavior testifies to the reliability of our technique.

Figure 5 benchmarks our measured data with those in the literature [15] and the manufacturer's data [20]. The solid line is the Tóth equation curve derived from experimental results measured via the constant-volume-variable-pressure (CVVP) technique [15]. It is palpable that the mutual agreement in trend is very good. The 5–10% mismatch between our current data and the data measured volumetrically at relatively high vapor pressures is within the measurement uncertainty of the two independent techniques. In addition, the putative adsorption of water vapor by the stainless steel vessel in the CVVP system might have contributed to the observed higher uptakes when the vapor approaches the saturation state. The manufacturer's data, shown as dashed lines, are consistently lower than the two independent groups of measurement. Nonetheless the trends are the same. This benchmarking exercise also confirms the efficacy of the Tóth equation in representing the experimental data.

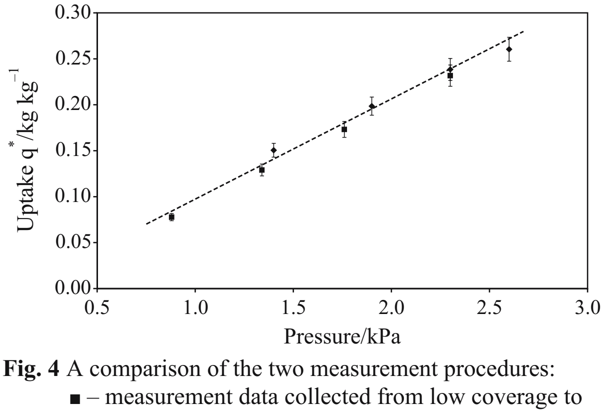

Fig. 4 A comparison of the two measurement procedures: ■ – measurement data collected from low coverage to high coverage, ◆ – measurement data collected from high coverage to low coverage

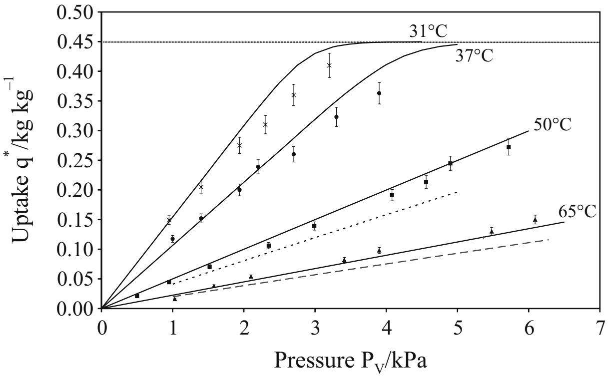

Fig. 5 Isotherms of water vapor adsorption on the type RD silica gel: solid lines are the Tóth correlation fitted from CVVP data [15] and the dashed lines are manufacturer's data [20]; the data points are our present measurements

Turning now to the ethanol-activated carbon system, Fig. 6 shows a set of experimental data of ethanol adsorption on the Maxsorp II activated carbon which has a specific surface area of around 3500 m^2 g^{-1} fitted by the Tóth equation. The Maxsorp II activated carbon has a very high affinity for ethanol and the maximum

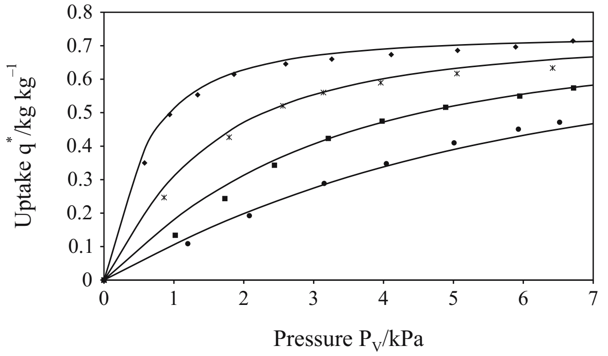

Fig. 6 Isotherms of ethanol adsorption on Maxsorp II activated carbon at different temperatures: solid lines are the best-fit Tóth correlation; ◆ – *T*=297.65K, × – *T*=313.15 K, ■ – *T*=338.15 K

Table 1 Correlation coefficients for the two different working pairs

Type	t	q_m/kg kg^{-1}	K_0/kg (kg kPa)$^{-1}$	$\Delta_{ads}H$/kJ kg^{-1}	Remarks
Water on RD silica gel	12	0.43	$7.3\cdot10^{-10}$	2690	By Tóth
Water on RD silica gel	12	0.45	$7.3\cdot10^{-10}$	2693	By Tóth [15]
Water on RD silica gel [20]			$2.0\cdot10^{-9}$	2510	By Henry
Ethanol on Maxsorp II activated carbon	1.45	0.73	$1.49\cdot10^{-8}$	967	By Tóth

uptake at near saturation condition can be as high as 72%. This suggests that the Maxsorp II activated carbon–ethanol system may be a promising candidate for the adsorption cooling system.

Table 1 showed the derived Tóth's parameters for the silica gel–water and Maxsorp II activated carbon–ethanol systems. For the silica gel–water system, the isosteric heat of adsorption is higher than that derived from the manufacturer's data [20] but is consistent with our independent measurements [15]. For the Maxsorp II–ethanol system, the maximum uptake is around 0.73 and the isosteric heat of adsorption is 967 kJ kg^{-1} which is about 10% higher than the ethanol latent heat of vaporization.

Conclusions

We have developed a thermogravimetric (TG) analyzer for condensable gas adsorption on solid adsorbents under subatmospheric conditions. Using this device, we have conducted equilibrium studies of water vapor on the Fuji Davison type RD silica gel and ethanol on the Maxsorp II activated carbon. For the water–silica gel system, we compare our measurements with the literature and manufacturer's data. A good agreement is found and testifies the reliability of our technique. We successfully use the Tóth equation to describe the isotherms of these two working pairs and derived the corresponding parameters. Those parameters will provide useful information for the manufacturers to design adsorption cooling systems and to better predict the system performance.

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