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Performance Prediction of Metal-Organic Frameworks (MOFs) based Desiccants for Adsorption Air-conditioning System

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SUMMARY

Metal-organic frameworks (MOFs) are a new class of porous crystalline materials with multiple and tuneable structures, which possess varieties of combinations from different metal clusters and organic ligands. Most MOF-based desiccants exhibit exceptional properties such as remarkable water vapour uptake capacity and gentle regeneration conditions, which make them very competitive for the adsorption air-conditioning system in comparison with conventional desiccants, for example, zeolite etc. The paper aims at investigating the performance of MOF-based adsorption system in comparison with the conventional zeolite-based system. The isotherms of MOF-based desiccants under different temperature have been investigated to estimate the equilibrium concentration of the adsorbed vapour. The experimental results indicate that there is more than 0.4 g/g of mass difference between 20 and 50 °C at 2000 Pa of water vapour pressure, which means the MOF-based adsorption cooling system can be powered by using low-grade energy around 50-70 °C temperature range. A mathematical model has been developed based on the general adsorption dynamics for a thin desiccant layer. Numerical simulations have been carried out to predict the change of adsorption dynamics under different vapour pressure. The results have shown that the MOF-based adsorption air-conditioning system powered by the low-grade energy exhibit higher operation performance in comparison with the traditional zeolite-based system.

KEYWORDS

Air conditioning, metal-organic framework (MOF), adsorption dynamic, hygrothermal transfer, mathematic model

1 INTRODUCTION

In the past decades, there have been growing interests in the adsorption-based air-conditioning system to satisfy the heat and cooling demand through using low-grade energy such as solar energy and waste heat. Compared with the conventional vapor-compression type systems, adsorption systems can take advantages of environmentally friendly adsorbates (i.e. water) and low-grade energy to ease the ozone depletion and global warming effect, which have no moving parts and vibration operation (Calm, 2002; Kim and Ferreira, 2008).

However, the drawbacks of adsorption systems include bulky size, low performance and high initial cost etc., limiting further popularization and commercialization (Ghazy, 2016). Actually, these problems is mainly caused by the lower loading lift during the operation cycles. The commonly used desiccants for air-conditioning systems are silica gel and zeolites, which suffer from high regeneration temperature and low loading lift at the low vapor pressure (Teo et al. 2017). Therefore, a large number of materials is required to reach the set operation capacity. Since the amount of loading lift in water uptake depends on the correlation between adsorption system and the properties of porous desiccant, it is an ongoing search for new materials with higher water uptake during adsorption cycles. Recently, some novel porous desiccants such as metal-organic framework (MOF) have gained much attention. Many experiments have indicated their superior performance in dealing with indoor hygrothermal loads to the desired conditions due to the high water uptake (i.e. water vapor) and low regeneration temperature (Cui et al. 2018; Lenzen et al. 2019). Therefore, the numerical study of MOF materials becomes necessary in order to predict the adsorption dynamics during cycles.

In this paper, the dynamic performance using aluminum fumarate (Al Fum) MOFs has been investigated through mathematical modelling analysis, and make comparisons with some conventional materials based on the same operation conditions to explore the feasibility of Al Fum in heat and humidity control.

2 METHODS

2.1 Water adsorption

The measurement of water uptake on Al Fum was obtained from a gravimetric analyser owing to the high accuracy in the temperature and humidity control during the whole experiments. Fig.1 has shown the schematic configuration of the apparatus. Prior to the measurements of adsorption dynamics experiments, the Al Fum sample was first dried in an oven at 150°C for at least 2h, and then hung on the microbalance at a temperature-controlled adsorption chamber. The isothermal environment around Al-MOF sample was required to be provided by the built-in-radiant heater. After the Al-MOF was loaded on the microbalance, the sample will undergo a heating process to be outgassed, and dry nitrogen (99.999% purity) will be continuously supplied to remove the released moisture at the same time. After the regeneration process was completed, the dried MOF sample was cooled to the given temperature condition.

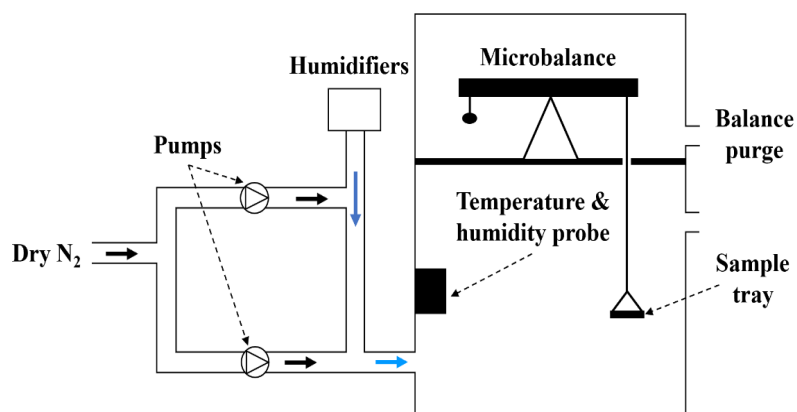


Figure 1. Schematic illustration of gravimetric analyser.

During the experiments, the continuous supply of N₂ can maintain the buoyancy of microbalance. A vacuum pump was turned on to maintain the pressure in the adsorption chamber. The control panel can automatically regulate the vapor charging flux supplied by an integrated humidifier unit to reach the set vapor pressure condition. To avoid the condensation effect, it is required that temperature in the adsorption chamber was maintained 15°C higher than the experimental conditions.

2.2 Mathematical model

The description of heat and mass transfer inside the porous desiccant is a complex problem involved many different mechanisms. Here, in order to predict the adsorption dynamics during adsorption cycles, a transient 2D model with adsorption rate and temperature change were developed. Fig.2 has shown a square-shaped Al Fum MOF sample (5mm*5mm) in a climate chamber with a set temperature and vapor pressure. Here, the governing equations to the overall transport can be divided into mass and energy conservation.

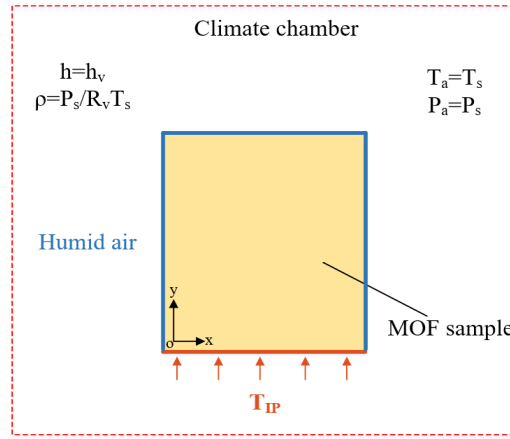


Figure 2. The configuration of the simulated model.

1) Mass conservation equations

Vapor transport between desiccant crystals can be written as (Chan et al. 2012):

$$\frac{\partial \rho_a}{\partial t} + \nabla \cdot (\vartheta \rho_a) = \nabla \cdot D_v \nabla \rho_a - \frac{1-\varepsilon}{\varepsilon} \frac{\partial C_\mu}{\partial t} \quad (1)$$

Where ρ_a is the vapor concentration for the intercrystalline voids [kg m^{-3}]; ε is the porosity of desiccant; C_μ is the concentration of the adsorbed vapor within the desiccant crystals, and $\frac{\partial C_\mu}{\partial t}$ represents the adsorption rate at a given time and space.

2) Energy conservation equations

The energy conservation for the desiccant layers can be given as (Chan et al. 2012):

$$\rho' c \left(\frac{\partial T}{\partial t} + \vartheta \nabla \cdot T \right) = \nabla \cdot \lambda_{eq} \nabla T + q_{st} \varepsilon \frac{\partial C_\mu}{\partial t} \quad (2)$$

Where q_{st} represents the adsorption heat during adsorption process. $\rho' c$ is the volumetric heat capacity calculated by $\overline{\rho' c_p} = (1-\varepsilon)\rho_m c_{pm} + (1-\varepsilon)\omega\rho_m c_{pw} + \varepsilon\rho c_{pv}$, which consists of

desiccant (c_{pm}), adsorbed vapor (c_{pw}) and vapor phase (c_{pv}). λ_{eq} is the equilibrium thermal conductivity.

3) Isotherms and kinetics model

In order to obtain the adsorption rate within the desiccant crystals, linear driving force (LDF) model is applied as (Sircar and Hufton, 2000):

$$\frac{dC_{\mu}}{dt} = \frac{60}{d^2} D_s (C_{\mu_{eq}} - C_{\mu}) \quad (3)$$

Where D_s stands for surface diffusion, and d is the diameter of desiccant particles. Here the equilibrium concentration of adsorbed vapor $C_{\mu_{eq}}$ is derived by Langmuir type isotherm, which is a function of temperature and vapor pressure. The details about Langmuir curves can be found in Ref. (Hefti et al. 2016).

3 RESULTS

The crystalline structure of Al Fum has a 3D cubic shape, composed of corner-sharing AlO_6 chains and terephthalate ligands, forming uniform mesoporous cavities of $\sim 6 \text{ \AA}$. The BET surface of Al Fum was measured equal to $970 \text{ m}^2/\text{g}$. Fig.3 shows the microstructure of this MOF sample by scanning electron microscope (SEM), illustrating the intercrystalline structures that allow the vapor transport within the desiccant.

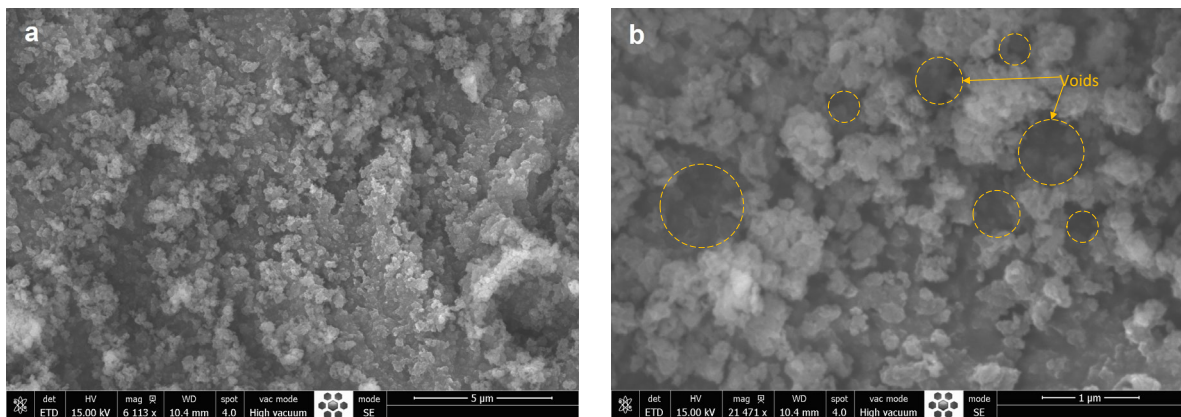


Figure 3. SEM of Al Fum sample showing intercrystalline structure.

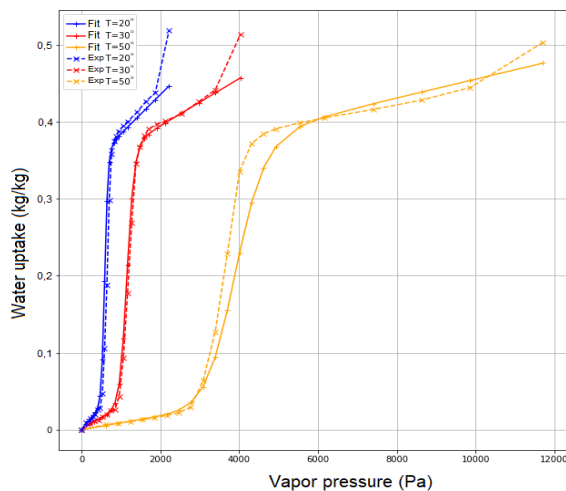


Figure 4. Measured and fitted water adsorption

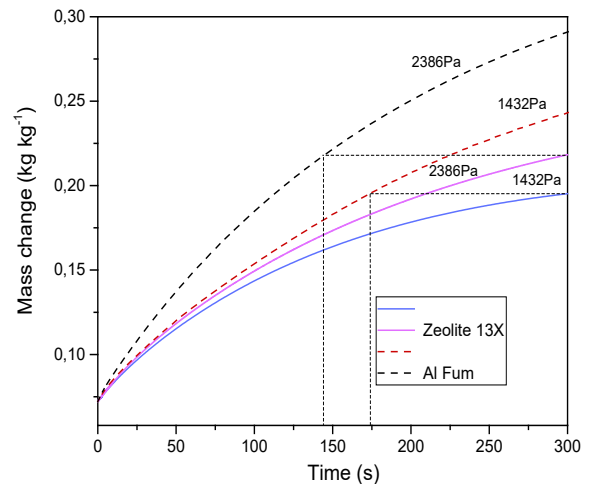


Figure 5. The simulated mass change of Zeolite

isotherms at 20°C, 30°C and 50°C.

13X and Al Fum during adsorption.

In order to obtain the equilibrium concentration of the adsorbed vapor, Langmuir fitting curves have been made as shown in Fig. 4. It can be found that the measured water uptake isotherms at different temperature (20°C, 30°C and 50°C) fit well with the fitting curves. The cyclic uptake is about 0.41kg/kg dry mass between 20°C and 50°C at 2000Pa, which indicates that it has a low water uptake capacity at a relatively high temperature and make use of low-grade heat source possible. Later on, the corresponding numerical study of adsorption dynamics have been conducted with two different vapor pressure condition (1432Pa and 2386Pa). Fig. 5 shows the adsorption dynamics of zeolite and Al Fum, which indicate a more than 0.28kg/kg of water uptake for Al Fum compared with that of 0.21 kg/kg for zeolite 13X under 2386Pa of vapor pressure. And it can only take less than 150s for Al Fum to reach the same amount of water uptake for Zeolite 13X at 300s.

4 DISCUSSION

Owing to the adsorption heat for those porous desiccants, it is hard to conduct an isothermal adsorption, which has been proved a more efficient method to the indoor humidity and temperature control. In this work, Table 1 has shown that the water uptake isotherm of Al Fum have a much higher value than Zeolite 13X at relatively low temperature range. This means that the adsorption capacity of Al-Fum is twice as that of zeolite 13X below 50°C, and the reason may be homogeneous crystal structure of Al Fum.

Table 1. The maximum amount of water uptake at different temperature.

Temperature	Zeolite 13X (Narayanan, 2014)	Al Fum
20°C	0.25kg/kg	0.52kg/kg
30°C	0.25 kg/kg	0.51kg/kg
50°C	0.25 kg/kg	0.5kg/kg

Table 2. The comparison of the simulated adsorption dynamics for Zeolite 13X and Al Fum.

	1432Pa	2386Pa
Zeolite 13X	300s (0.19 kg/kg)	300s (0.22kg/kg)
Al Fum	174s (0.19 kg/kg)	145s (0.22kg/kg)

When giving the same operation condition, it can be seen that Al Fum has a larger adsorption rate based on the numerical results, and needs less operation time to remove the humidity load. Therefore, it is potential to bring a higher dehumidification rate for Al Fum than zeolite 13X. Recently, Kummer (2017) have made a full-scale heat exchanger coated with Al Fum, and the results have indicated the fast adsorption kinetics compared to conventional desiccants. Thus, the air-conditioning system using Al Fum MOF is competitive with most commercial cooling systems.

5 CONCLUSIONS

Al Fum desiccant can achieve the heat and mass transfer among the air, desiccant and cooling medium. The experimentally measured water uptake can achieve a 0.41kg/kg of loading lift in isotherms. Given the same adsorption conditions, the cyclical water uptake of Al Fum well outperforms most of conventional desiccants, which indicate a strong capacity to control the humidity load with less time. In addition, assumed that the boundary temperature in the bottom side of Al Fum was maintained at a set value, the numerical studies have shown that adsorption performance of Al Fum is superior to that of zeolite 13X. The numerical results of

adsorption dynamics prove that Al Fum MOF is a promising candidate in the isothermal adsorption.

6 ACKNOWLEDGEMENT

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