

# Assessment of adsorption-desorption characteristics of adsorbents for adsorptive desiccant cooling system

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The performance of various dehumidification materials was assessed in terms of effective adsorption amount of water vapor based on the adsorption isotherms to find a suitable dehumidification element for an economical adsorptive desiccant cooling system being developed. The effective adsorption amount is an important factor for regeneration at lower temperatures. Three types of silica gels, S(a), S(b), and S(c), with different pore volumes and pore size distributions, and zeolite with various molar ratios of Si/Al, 5.6, 29, 47, 91, and 220, prepared from a Y-type zeolite treated with hydrochloric acid, an activated carbon with silica gel added to improve the hydrophobic surface, and MCM-41 were examined. Silica gels having effective adsorption amounts of 0.25 g/g, and activated carbon with silica gel added were assessed to be candidate desiccant materials.

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## 1. Introduction

An adsorptive desiccant cooling system and dehumidifier, which are operated by heat swing process, have recently been studied based on repetition of adsorption and desorption, as opposed to an air conditioner working with refrigerants. These instruments are becoming attractive for their energy savings.

Our previous papers [1, 2] investigated the assessment parameters of the dehumidification performance of desiccant elements for an adsorptive desiccant cooling system working at lower temperatures and/or lower heat quantities. The experiments and evaluations were conducted using a dehumidifier with a desiccant element operating in a rotary and a countercurrent system. Two kinds of corrugate-type desiccant elements, silica gel and zeolite, were chosen to compare the differences in performance. Consequently, we found a linear relationship between the dehumidification amount and the heat quantity for regeneration when the partition ratio, implying the ratio of adsorption to desorption areas as constant, and the wind velocities of both areas were identical at optimum rotational speed. The heat quantity was found to be low when the element adsorbed at a lower partition ratio was regenerated.

A previous paper [2] performed a simulation to systematize the air conditioner operating with heat-swing process using various parameters and the adsorption-desorption characteristics of the desiccant elements.

The simulation results confirmed that the performance of the dehumidification system could be evaluated from the adsorption-desorption characteristics of the desiccant elements. Therefore, the simulation was recognized to be a useful tool for selecting desiccant elements and design apparatuses.

A few studies on evaluating characteristics of desiccant materials [3, 4] and improving dehumidification performance of elements [5, 6] have been reported and silica gel, zeolite, and activated carbon are candidates for desiccant materials. Silica gel is superior to zeolite in that desorption is possible at relatively low temperatures [7]. Zeolite needs to be desorbed at high temperatures, though the moisture can be reduced to lower dew points. The adsorption-desorption characteristics depend on the kind of silica gels and also the difference between hydrophilic and hydrophobic surfaces of zeolite. Therefore, these items must be considered when selecting a desiccant material (adsorbent) suitable as an element in a dehumidifier.

The authors have evaluated the performance of various desiccant materials on the market and optimized equipment using dehumidification elements such as silica gels and zeolite, aiming at a developing an economical adsorptive desiccant cooling system. This paper reports the basic knowledge of the adsorbent characteristics required to achieve regeneration at lower temperatures.

## 2. Experimental

### 2.1. Adsorbents as desiccant materials

#### 2.1.1. Silica gels

Three types of silica gels, S(a), S(b), and S(c), (Fuji Silisia Chemical Co., Ltd., Japan), with different pore volumes and pore size distributions were employed. S(a) is grade A 5-10 (“type A”), S(b) is grade B 10-20 (“type B”), and S(c) is grade RD on 8 (“type RD”).

#### 2.1.2. Zeolites

The regeneration of zeolites at low temperatures is difficult because the bond of water molecules with cation sites based on Al in zeolite is quite strong. However, the surfaces of Y-type zeolite can be converted from hydrophilic to hydrophobic through reduction of Al by treating it with an acid. This reduction of Al concentration in zeolite enables regeneration at low temperatures. In this sense, we were interested in the effect of Al concentration on adsorption and desorption of water vapor. In this study, zeolites with the molar ratios (Si/Al) of 5.6 (Z(a)), 29 (Z(b)), 47 (Z(c)), 91 (Z(d)), and 220 (Z(e)) were prepared from Y-type zeolite (produced by TOSO Co. Ltd., Japan).

#### 2.1.3. Activated carbons

There is a tendency for activated carbons to abruptly decrease in adsorption amounts at low relative pressures (RHs) of water vapor because of the surfaces being hydrophobic. Therefore, activated carbon can not be expected to serve as a desiccant material. In this study, the addition of silica gel to an activated carbon was examined to improve the hydrophobic surface. An activated carbon (AC(a)) made from coconut shell (produced by Hokuetsu Tanso Co., Ltd., Japan) was selected. AC(a) is grade Y-60. The activated carbon, adjusted to sizes of 0.15 to 0.30 mm, was soaked in a solution of 1 wt% Na<sub>2</sub>SiO<sub>3</sub> to deposit SiO<sub>2</sub> component at 30°C for 72 h. The activated carbon was dried at 120°C for 2 h after filtrating and rinsing with water, and treated with sulfuric acid solution of 3.9 mol/dm<sup>3</sup> at 30°C for 24 h to convert SiO<sub>2</sub> into silica gel. This activated carbon will be referred to as AC(b) in this paper.

#### 2.1.4. Mesoporous silicate

Mesoporous silicate has a large volume consisting of almost homogeneous pore size. Some studies have been conducted on MCM-41 and FSM-16 [8, 9]. In our current study, we synthesized MCM-41 to assess its characteristics as a desiccant material. The synthesis method [10] was as follows. Tetraethoxy silane (TEOS, produced by Aldoritch Co., Ltd.) was used as a source of silica, and *n*-tetradecyl trimethyl ammonium bromide (C16N, Aldorich), as a template material. A C16N solution of 0.055 mol/dm<sup>3</sup> was prepared by dissolving C16N into 120 g of distilled water. Ammonium solution (9.5 g; 25 wt%) was then added to the C16N solution, and 10 g of TEOS (98 wt%) was dropped in within 15 min. The precipitate that formed was recovered by filtration and rinsed with distilled water of 1 dm<sup>3</sup>. It was then dried at 90°C, and MCM-41 was obtained by

TABLE I Effective adsorption amount of water vapour by various adsorbents

Material	Specimen	Effective adsorption amount (g/g)	Amount of water vapor adsorption (g/g) at 0.60 (RH)	Amount of water vapor adsorption (g/g) at 0.07 (RH)
Silica gel	S(a)	0.28	0.33	0.05
	S(b)	0.06	0.08	0.02
	S(c)	0.31	0.36	0.05
Zeolite	Z(a)	0.05	0.30	0.25
	Z(b)	0.13	0.17	0.04
	Z(c)	0.05	0.05	0.0
	Z(d)	0.02	0.02	0.0
	Z(e)	0.02	0.02	0.00
Activation carbon	AC(a)	0.18	0.18	0.0
	AC(b)	0.25	0.29	0.4
Mesoporous silicate	MCM-41	0.39	0.46	0.07

firing at 550°C for 5 h in air. The heating rate from room temperature to 550°C was 1°C/min. The surface of mesoporous silicates such as MCM-41 is known to become hydrophilic once it has adsorbed water vapor [11]. The reason seems to be that siloxane bond on the surface of silica is hydrolyzed by adsorbing water to be converted into silanol group which is advantageous to further adsorption of water molecule.

The specimens employed in this study are listed in Table I.

### 2.2. Measurement of water vapor adsorption isotherm

Water vapor adsorption isotherms were investigated to evaluate the characteristics of adsorbents. A 0.2 g sample of each adsorbent was weighed, placed in a sample tube, and heat-treated at 150°C in vacuum for 5 h. Isotherms at 25°C were measured using BELSORP18 (Japan Bell Co., Ltd.).

### 2.3. Measurements of BET surface area and pore size distribution

Nitrogen isotherms on the adsorbents were measured at -196°C using the instrument mentioned above. The surface area was calculated by the BET technique. Pore size distributions of each adsorbent were calculated from the nitrogen isotherms by the Dollimore-Heal method [12] at more than 2 nm and the Micro Pore Analysis method at less than 2 nm. The distribution was explained using the relation between the derivative  $dV/dRb$  and pore diameter  $2Rp$ . Here,  $V$  indicates pore volume, and  $Rb$ , pore radius.

## 3. Results and discussion

### 3.1. Water vapor adsorption isotherms of various adsorbents

The performance of dehumidifier adsorbents is not always assessed by the adsorption amount alone. Adsorbents should also have a large difference in adsorption amounts between adsorption and desorption. For example, when adsorption condition is RH of 0.60 at 27°C

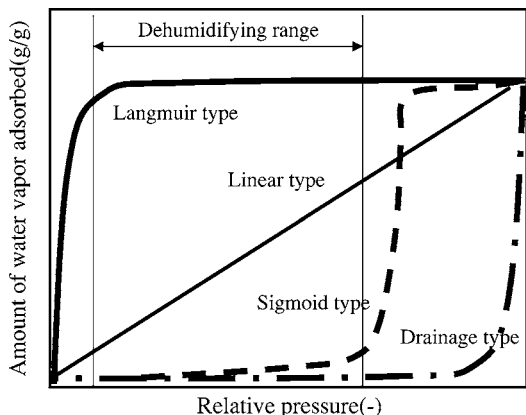


Figure 1 Water vapor adsorption isotherms.

and regeneration is selected to be set at 70°C, the RH in the environment for regeneration is reduced to around 0.07. The difference in the adsorption amounts (effective adsorption amount) between RH of 0.60 and 0.07 represents the adsorbent's ability to treat water vapor in the air. Since the adsorption isotherms obtained at different temperatures are standardized by RH [13, 14], we can establish the effective adsorption amount and the performance of the adsorbent from isotherms of water vapor. Therefore, we focused on the isotherms but recognized that the rates of adsorption-desorption must be considered when evaluating performance.

Typical isotherms are illustrated in Fig. 1. Isotherm of silica gel tends to be linear, isotherm of zeolite tends to be the Langmuir type, isotherm of activated carbon tends to be drainage, and isotherm of mesoporous silicate tends to be sigmoid [15]. Since mesoporous silicates generally have a large hysteresis, the effective adsorption amount was evaluated from adsorption-desorption isotherms.

### 3.1.1. Silica gels

Figs 2 and 3 depict the pore size distributions and the isotherms of silica gels. Specimen S(a) has a sharp pore size distribution around 1 nm. The distribution type of S(c) is almost same as that of S(a). However the peak position of S(c) is shifted to smaller size. The distribution of S(b) shows a broadening peak in the range from 2 to 10 nm and it has no pores with size of less than 2 nm. The isotherms of S(a) and S(c) are almost linear and that of S(b) is sigmoid. The isotherms shown in

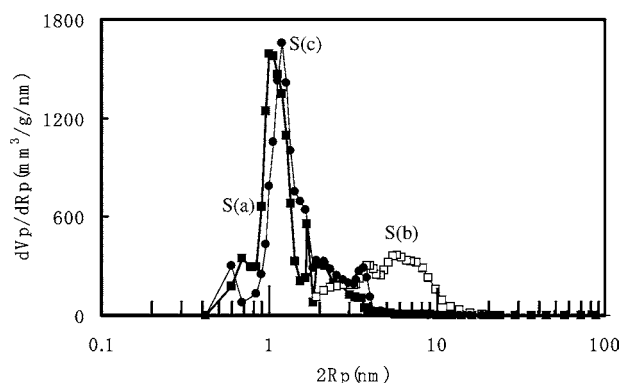


Figure 2 Pore size distributions of silica gels.

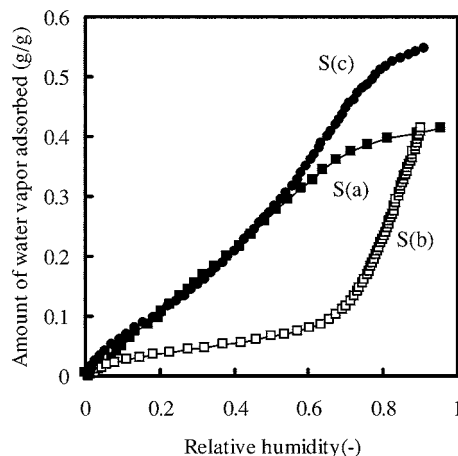


Figure 3 Water vapor adsorption isotherms on silica gels.

Fig. 3 were confirmed to be almost the same as moisture isotherm printed in the manufacture's catalogue. Chua *et al.* [16] have reported the water vapor adsorption isotherms on type A and type RD silica gels. These type of silica gels correspond to specimens S(a) and S(c) used in this work. Their data show that the adsorption isotherms of S(a) and S(c) resemble to those of type A and type RD in terms of the shape of isotherm. Further, it was observed that the pore size distributions of S(a) and S(c) specimens were almost equal to the type A and type RD of which the distributions were analyzed by DFT method. From these views, the distributions obtained by means of MP and DH methods are considered to be valid to assess the pores available to water vapor adsorption.

The amounts of water vapor adsorbed on S(c) at higher RHs exceeds that on S(a), whereas the amounts adsorbed at lower RHs are almost the same. The adsorption amount of S(b) abruptly rises at RHs exceeding 0.7. The effective adsorption amounts are evaluated as 0.28 for S(a), 0.06 for S(b), and 0.31 for S(c). The effective adsorption amount of S(a) is near to that of S(c), which is coherent to the fact that the pore size distribution of S(a) and S(c) resemble each other. The pore volume with pore sizes of less than 2 nm in S(b) is less than pore volumes in S(a) and S(c), but the region with pore sizes of 5 to 20 nm is larger than for S(a), and S(c). Therefore, pore volume with pore sizes less than 2 nm is speculated to be related to the adsorption amount at lower RHs.

### 3.1.2. Zeolites

Fig. 4 illustrates the isotherms of water vapor on zeolites with various ratios of Si/Al. It is clear that the ratio of Si/Al strongly affect the isotherm type. Although the Zeolites with high Si/Al ratios, Z(c), Z(d) and Z(e), adsorb low amounts at lower RHs, but the amount steeply increases with increasing ratio at higher RHs. These patterns indicate hydrophobic adsorbents as generally seen. The decrease in Al content proves that the zeolite loses hydrophilicity. The isotherm on Z(b) is the Henry type displaying an almost linear relation. Z(a) has the lowest ratio and exhibits a Langmuir type isotherm. The effective adsorption amounts were 0.05 for Z(a), 0.13 for Z(b), 0.05 for Z(c), 0.02 for Z(d), and 0.02 g/g for

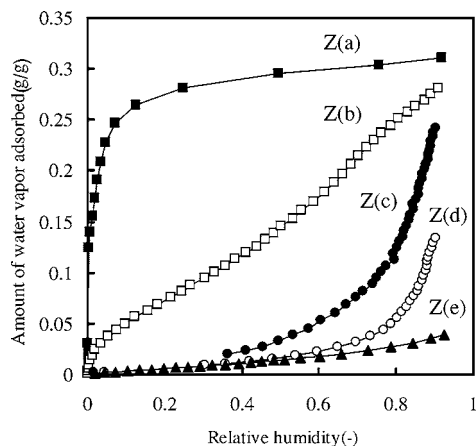


Figure 4 Water vapor adsorption isotherms on zeolites.

Z(e). Z(b), which has a linear type isotherm as shown in Fig. 1, adsorbed the highest amount.

### 3.1.3. Activated carbons

Fig. 5 illustrates the pore size distributions of AC(a) and AC(b). The distribution curves are almost identical. Therefore, the microstructure was not changed by treatment for hydrophilic surfaces. Fig. 6 presents the isotherms for AC(a) and AC(b). The isotherm of AC(a) is a typical hydrophobic type, indicating that the amount adsorbed steeply increases at higher RHs. Consequently, adsorption at lower RHs is low but abruptly

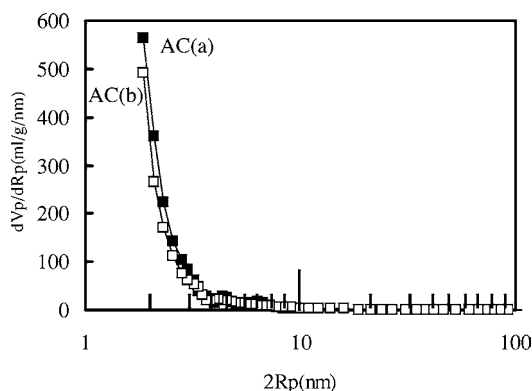


Figure 5 Pore size distributions of activated carbons.

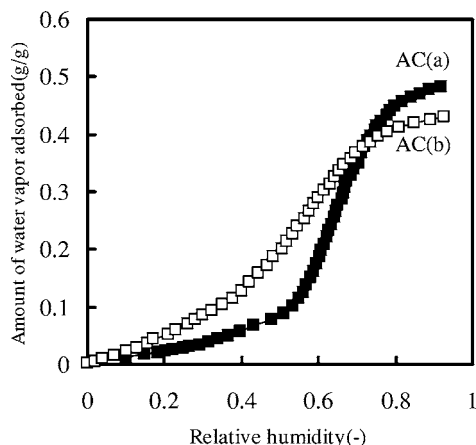


Figure 6 Water vapor adsorption isotherms on activated carbons.

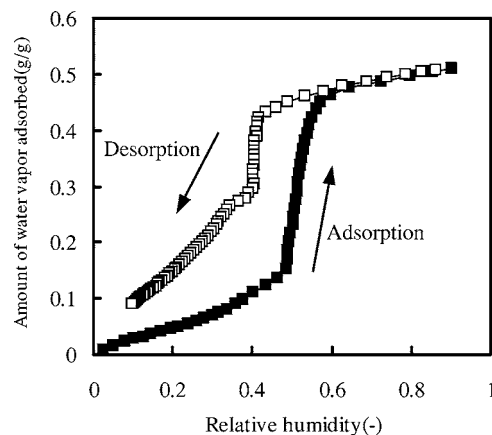


Figure 7 Water vapor adsorption-desorption isotherms on MCM-41.

rises at higher RHs where the effective adsorption amount reaches 0.18 g/g. However, this is not considered to be large enough. The isotherm of AC(b) exhibits improved adsorption in the intermediate region, and the effective adsorption amount is 0.25 g/g. This is due to treating for activated carbon to obtain a hydrophilic surface. Consequently, the effective adsorption amount is significantly improved compared to AC(a) because the linearity of the isotherm becomes better. Therefore, the formation of silica gel in pores of activated carbon effectively improves the adsorption pattern.

### 3.1.4. MCM-41

Fig. 7 illustrates the adsorption-desorption isotherms of water vapor on MCM-41. A large hysteresis loop exists over a wide range, and both curves are sigmoidal. The effective adsorption amount is evaluated to be 0.39 g/g, suggesting that MCM-41 is a promising material. However, MCM-41 and monoporous silicate adsorption characteristics become hydrophilic once they adsorb water or water vapor and have poor mechanical strength and durability.

## 3.2. Comparison of effective adsorption amount

The capacity of general adsorbents must be high. However, the adsorbent performance as a desiccant material used in thermal swing adsorption systems must be evaluated by the differences in adsorption amount between high RHs and low RHs, i.e., the effective adsorption amount. In this paper, 0.6 RH (27°C) and 0.07 RH (70°C) were selected as a practical adsorption and regeneration values. The difference was assessed directly from the isotherms measured at 25°C, separately from the strict discussion. The effective adsorption amounts of specimens in this work are listed in Table I. S(a), S(c), AC(b) and MCM-41 are likely candidates for desiccant materials because they have a relatively large effective adsorption amount. In contrast, the absolute adsorption amounts of zeolites are low, although the effective adsorption amount can be increased by making surfaces hydrophobic. However, use in a dehumidification instrument will require large quantities.

#### 4. Conclusion

This paper assessed the performance of various dehumidification materials on the market in terms of effective adsorption amount of water vapor as an important factor for regeneration at lower temperatures. The characteristics of water vapor adsorption are summarized as follows.

1. Three types of silica gels, S(a), S(b), and S(c), with different pore volumes and pore size distributions were examined. The effective adsorption amounts were evaluated as 0.28 g/g for S(a), 0.06 g/g for S(b), and 0.31 g/g for S(c).

2. Zeolites with molar ratios of Si/Al, 5.6, 29, 47, 91, and 220, were prepared from a Y-type zeolite. The effective adsorption amounts for these resultant zeolites were evaluated to be 0.05 g/g for an Si/Al ratio of 5.6, 0.13 g/g for an Si/Al ratio of 29, 0.05 g/g for an Si/Al ratio of 47, 0.02 g/g for an Si/Al ratio of 91, and 0.02 g/g for an Si/Al ratio of 220. The isotherm of the specimen with molar ratio of 29 was found to be Henry type and it had the highest effective adsorption amount among the resultant zeolites.

3. An activated carbon with silica gel added to improve the hydrophobic surface was prepared. The effective adsorption amount was 0.25 g/g, whereas the original activated carbon was 0.18 g/g. This is due to converting the surface to hydrophilic from hydrophobic by forming silica gel inside of the activated carbon.

4. The effective adsorption amount of MCM-41 was evaluated to be maximum at 0.39 g/g. However, this material is not a promising dehumidifier because it is altered to hydrophilic surface through adsorption of water or water vapor.

5. Silica gel having an effective adsorption amount of 0.25 g/g and activated carbon with silica gel added were assessed to be candidates for desiccant materials.

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