Adsorption Equilibrium of Water Vapor on F-200 Activated Alumina

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Adsorption isotherm data for water vapor on F-200 7 × 14 Tyler mesh activated alumina are obtained at (5, 15, 25, and 35) °C in the range 0% to approximately 95% relative humidity using a static gravimetric technique. F-200 is a commercially available adsorbent that has become very popular in industry for drying compressed air via pressure or temperature swing adsorption. The equilibrium isotherms are presented in tabular as well as in graphical form. The equilibrium data are measured in both directions: adsorption and desorption. A pronounced hysteresis between the adsorption and the desorption legs is present at all temperatures. When plotted versus the relative humidity, the equilibrium data are essentially independent of temperature. The complete removal of the adsorbed water requires regeneration at elevated temperature (290 °C) under vacuum. The data reported in this study can be used in industrial design as well as in the theoretical studies on the adsorption/desorption mechanisms of water vapor on activated alumina.

Introduction

Adsorption of water vapor from gaseous streams by solid adsorbents is an important industrial operation. In many cases, dehydration by adsorption achieves much lower dew points and is less energy demanding than other dehydration methods such as compression and condensation. Three classes of adsorbent materials are generally used in the drying of industrial gases by adsorption: activated alumina, silica gel, and molecular sieves. Activated alumina desiccants are widely applied in the drying of compressed air, natural gas, and saturated hydrocarbons.

Despite its wide use in adsorption-based drying applications, basic data for the adsorption/desorption equilibrium of water vapor on activated alumina have not been widely reported. The most comprehensive study was done by Desai et al.,[1] who investigated the equilibrium behavior of several types of commercially available activated alumina through a combined Langmiur/BET model. The equilibrium measurements were carried out by static gravimetric and breakthrough techniques. Kotoh et al.[2] developed a multilayer model for water adsorption on activated alumina and used it to correlate several sets of data that were obtained by dynamic gravimetric measurements. Carniglia and Ping[3] reported several sets of adsorption isosteres. From these three studies only the first one[1] shows the hysteresis loop between the adsorption and the desorption isotherms.

In recent years one type of activated alumina with the trade name F-200 is rapidly becoming the industry standard for drying compressed air. It is used in both thermal swing adsorption (TSA) mode and in pressure swing adsorption (PSA) mode. The efficient design of PSA and TSA units utilizing F-200 activated alumina requires knowledge of its equilibrium capacity for water vapor at various temperatures. Unfortunately, such data does not exist in the open literature. Data from previous studies[1−3]

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Table 1. Physical Properties of F-200 7 × 14 Tyler Mesh Activated Alumina Adsorbent as Reported by the Manufacturer

form	spherical
diameter	2 mm
surface area	360 m$^2 \cdot$g^{-1}
total pore volume	0.5 cm$^3 \cdot$g^{-1}
packed bulk density	769 kg$\cdot$m^{-3}

cannot be used because they are for other types of activated alumina and different activated alumina adsorbents have quite different adsorption properties.[1]

The aim of this work is to present experimental isotherms of water vapor on F-200 activated alumina at several temperatures. The equilibrium measurements are carried out by the static gravimetric technique. Complete adsorption and desorption isotherms are measured at (5, 15, 25, and 35) °C with the hysteresis loop clearly shown. The results are presented in tabular as well as in graphical form. Two different graphical representations are offered. The data can be used not only in the industrial design of PSA and TSA units but also in the development of theoretical models describing the adsorption/desorption of water vapor on activated alumina. Therefore, the experimental results reported in this study are of interest to both basic and applied research.

Experimental Section

Materials. The F-200 7 × 14 Tyler mesh size activated alumina is manufactured by Alcoa and is commercially available. The characteristics of the F-200 adsorbent used in this study are listed in Table 1 as reported in the manufacturer's specifications for the lot. Several samples from the lot were tested for surface area and total pore volume, and the results were consistent with the data reported by the manufacturer. The water used was high purity HPLC grade.

Equipment. The adsorption equilibrium data presented in this study were obtained by the static gravimetric tech-
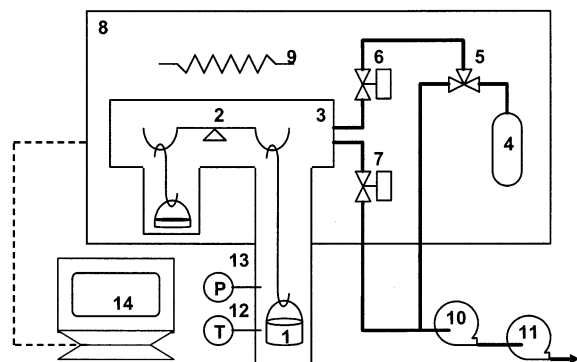
Figure 1. Schematic diagram of the IGA-002 apparatus for measuring adsorption equilibrium isotherms by the static gravimetric technique: 1, sample bucket; 2, microbalance; 3, reactor vessel; 4, liquid reservoir; 5, three-port isolation valve; 6 and 7, pressure control motor valves; 8, thermostatic cabinet; 9, heating element; 10, rotary vacuum pump; 11, turbomolecular vacuum pump; 12, thermometer; 13, manometer; 14, PC for experiment control and data acquisition.

nique. The adsorption equipment was an IGA-002 (intelligent gravimetric analyzer) system manufactured by Hiden Analytical, Ltd. (U.K.). This is a fully computer controlled apparatus designed for gravimetric measurements of adsorption and desorption. A schematic of the experimental setup is shown in Figure 1. A bucket filled with adsorbent material (1) is suspended on one of the arms of a microbalance (2) enclosed in a stainless steel reactor vessel (3). The microbalance has a sample capacity of 200 mg and a weighing resolution of 0.1 μg. The water vapor is supplied to the sample in the reactor from a 25 mL stainless steel reservoir (4) filled with liquid water. The upper portion of the reactor (3), the liquid reservoir (4), the three-port isolation valve (5), and the two pressure control motor valves (6, 7) are enclosed in a thermostatic cabinet (8). A heating element (9) is used to keep a constant temperature in the cabinet (8) such that sufficient vapor pressure is generated by the water in the reservoir (4). In adsorption/desorption mode the three-port isolation valve (5) enables the introduction of water vapor from the liquid reservoir to the reactor while in regeneration mode it isolates the liquid reservoir and enables the outgassing of the reactor and the vapor lines. The system is equipped with a primary oil-free rotary vacuum pump (10) and a secondary ultrahigh vacuum turbomolecular pump (11). The two pumps work in series and can attain a vacuum of 10^{-6} mbar. The pressure in the reactor is maintained by motor valves 6 and 7. If the pressure in the reactor is above the set point, motor valve 7 opens to remove the excess water vapor out of the reactor. If the pressure in the reactor is below the set point, motor valve 6 opens to admit additional water vapor into the reactor. The temperature in the vicinity of the sample is measured by a platinum resistance thermometer (12) with an accuracy of ±0.1 °C. The pressure in the reaction chamber is measured by a capacitance manometer (13) with a range of 100 mbar and an accuracy of ±0.02 mbar. A liquid jacket (not shown in the schematic) is placed around the lower part of the reactor to maintain the desired sample temperature during adsorption/desorption. The liquid in the jacket is recirculated through a refrigerating/heating bath (not shown in the schematic). The liquid jacket is replaced by a laboratory furnace (not shown in the schematic) during sample regeneration. The temperature control is able to maintain the set point temperature in the vicinity of the sample within 0.1 °C. A personal computer (14) is used for control and data acquisition.
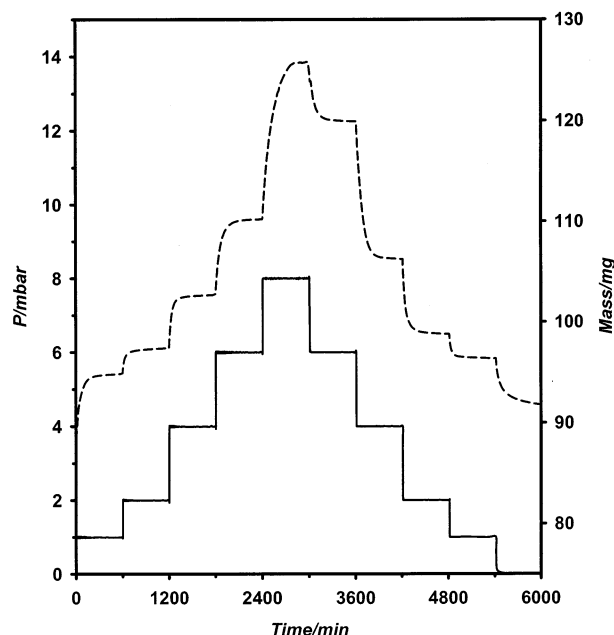

Figure 2. Typical plot of the data acquired during an adsorption/desorption experiment at constant temperature. Data at 15 °C. —, pressure; - - -, sample mass.

Procedure. A known mass of the adsorbent (85–100 mg dry mass) was placed into the sample bucket. The reactor was sealed, and the laboratory furnace was placed around it. The sample was regenerated under vacuum (10^{-6} mbar) at 290 °C for 48 h. To prevent boiling, the temperature was ramped at a rate of 3 °C/min. The regeneration temperature was determined by trial and error using a procedure similar to the one described by Desai et al.[1] The mass of the sample at the end of regeneration was recorded as the dry mass of the sample. Upon regeneration, the furnace was replaced with a liquid jacket and the desired temperature for the adsorption/desorption experiment was set. The temperature in the thermostatic cabinet was set usually 10 °C higher than the sample temperature. The isotherm started from vacuum conditions. The pressure was increased stepwise until the highest pressure on the isotherm was reached and then decreased in the same manner back to vacuum conditions. Each pressure level was maintained for 10 h. The mass of the sample was constantly monitored and recorded, taking into account the buoyancy correction. A typical plot of the experimental data is shown in Figure 2. At the end of each 10-h period there was virtually no change observed in the mass of the sample, and this was recorded as the equilibrium mass. Upon completion of the adsorption/desorption sequence the sample was regenerated and used for another adsorption/desorption experiment at a different (or the same) temperature.

Results and Discussion

The adsorption isotherm data for water vapor on F-200 7 × 14 Tyler mesh activated alumina were obtained at (5, 15, 25, and 35) °C in the range 0% to approximately 95% relative humidity. Due to condensation at the reactor walls in contact with the cooling liquid, sustainable pressure control was difficult to achieve for relative humidity above 95%.

The adsorption isotherm data are presented in Figures 3–6 and Tables 2–5. All isotherms are type IV according to the Brunauer classification.[4] There is a pronounced
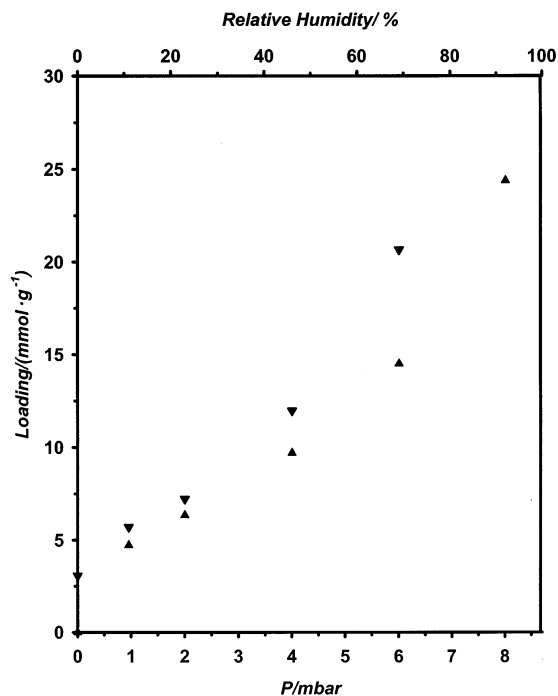
Figure 3. Equilibrium isotherm for water vapor on F-200 7 × 14 Tyler mesh activated alumina at 5 °C: ▲, adsorption; ▼, desorption.
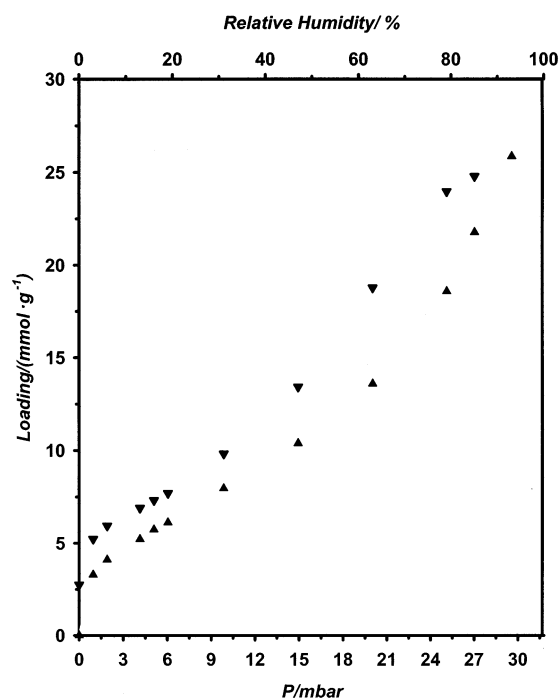

Figure 5. Equilibrium isotherm for water vapor on F-200 7 × 14 Tyler mesh activated alumina at 25 °C: ▲, adsorption; ▼, desorption.
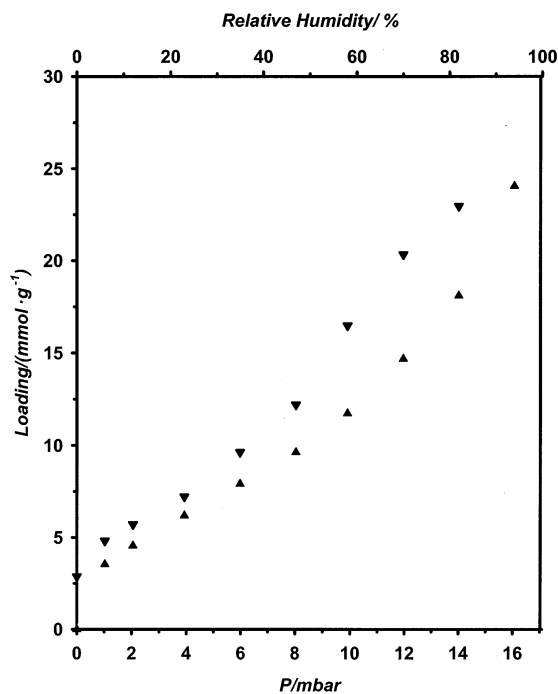

Figure 4. Equilibrium isotherm for water vapor on F-200 7 × 14 Tyler mesh activated alumina at 15 °C: ▲, adsorption; ▼, desorption.
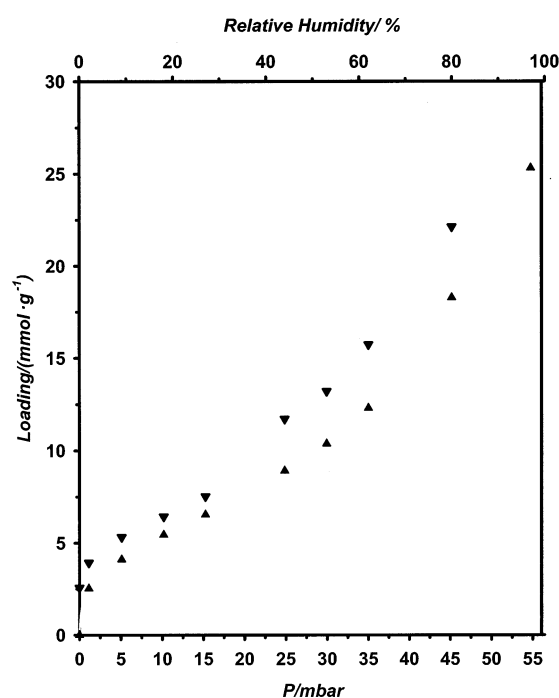

Figure 6. Equilibrium isotherm for water vapor on F-200 7 × 14 Tyler mesh activated alumina at 35 °C: ▲, adsorption; ▼, desorption.

hysteresis between the adsorption and desorption legs of the isotherm, which is consistent with previous results in the literature.[1] The steepest part in the isotherms is in the range above 40% relative humidity. This is the same range in which the hysteresis is most pronounced. These two effects are related and are caused by filling and emptying of the mesopores by capillary condensation.

In pressure swing adsorption (PSA) operations the presence of a hysteresis in the adsorption isotherm translate into reduced working capacity of the adsorbent. The design of many PSA operations neglects this effect and is based only on the adsorption leg of the isotherm. However, if the regeneration conditions are such that the relative humidity in the bed is above 40%, the decrease in the working capacity cannot be neglected and the PSA design must be based on both legs of the isotherm.

Evacuation alone does not remove all of the adsorbed water. The residual loading at the end of each adsorption/desorption experiment ($P = 10^{-6}$ mbar) is representative of the amount of chemisorbed water. It does not change

Table 2. Isotherm Data for Water Vapor on F-200 7 × 14 Tyler Mesh Activated Alumina at 5 °C

P/mbar	rel humidity/%	loading/mmol·g^{-1}
	Adsorption	
10^{-6}	0.00	0.0000
1.00	11.49	4.7265
2.00	22.97	6.3437
4.00	45.94	9.7004
6.00	68.92	14.4960
8.00	91.89	24.3822
	Desorption	
6.00	68.92	20.6559
4.00	45.94	11.9711
2.00	22.97	7.2246
1.00	11.49	5.7063
10^{-6}	0.00	3.0722

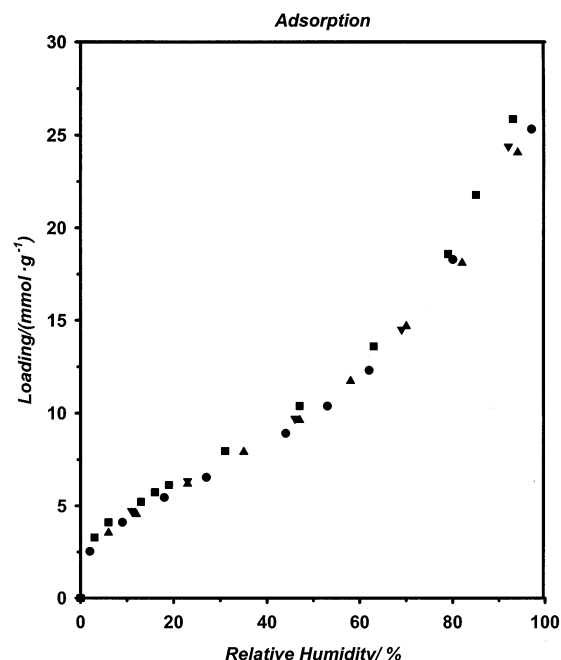**Table 3. Isotherm Data for Water Vapor on F-200 7 × 14 Tyler Mesh Activated Alumina at 15 °C**

P/mbar	rel humidity/%	loading/mmol·g^{-1}
	Adsorption	
10^{-6}	0.00	0.0000
1.00	5.85	3.5374
2.00	11.71	4.5507
4.00	23.42	6.1894
6.00	35.13	7.9134
8.00	46.84	9.6300
10.00	58.55	11.7333
12.00	70.25	14.6807
14.00	81.96	18.0958
16.00	93.67	24.0555
	Desorption	
14.00	81.96	22.9594
12.00	70.25	20.3320
10.00	58.55	16.4763
8.00	46.84	12.1969
6.00	35.13	9.6264
4.00	23.42	7.2109
2.00	11.71	5.7087
1.00	5.85	4.8140
10^{-6}	0.00	2.8763

Table 4. Isotherm Data for Water Vapor on F-200 7 × 14 Tyler Mesh Activated Alumina at 25 °C

P/mbar	rel humidity/%	loading/mmol·g^{-1}
	Adsorption	
10^{-6}	0.00	0.0000
1.00	3.15	3.2889
2.00	6.29	4.1098
4.00	12.58	5.2186
5.00	15.73	5.7357
6.00	18.88	6.1206
10.00	31.46	7.9612
15.00	47.19	10.3854
20.00	62.92	13.5932
25.00	78.65	18.5830
27.00	84.94	21.7738
29.50	92.80	25.8567
	Desorption	
27.00	84.94	24.7804
25.00	78.65	23.9662
20.00	62.92	18.7762
15.00	47.19	13.4201
10.00	31.46	9.8221
6.00	18.88	7.7036
5.00	15.73	7.3174
4.00	12.58	6.9036
2.00	6.29	5.9448
1.00	3.15	5.2281
10^{-6}	0.00	2.7468

significantly in the investigated temperature range. At 5 °C the residual loading is 3.0722 mmol/g while at 35 °C it is 2.5690 mmol/g. Much higher temperature (290 °C) at vacuum conditions was needed during regeneration in

Figure 7. Equilibrium loading (adsorption) versus relative humidity for water vapor on F-200 7 × 14 Tyler mesh activated alumina at multiple temperatures: ▼, t = 5 °C; ▲, t = 15 °C; ■, t = 25 °C; ●, t = 35 °C.

Table 5. Isotherm Data for Water Vapor on F-200 7 × 14 Tyler Mesh Activated Alumina at 35 °C

P/mbar	rel humidity/%	loading/mmol·g^{-1}
	Adsorption	
10^{-6}	0.00	0.0000
1.00	1.77	2.5297
5.00	8.86	4.1091
10.00	17.72	5.4487
15.00	26.57	6.5407
25.00	44.29	8.9127
30.00	53.15	10.3761
35.00	62.00	12.3026
45.00	79.72	18.2836
54.90	97.26	25.3190
	Desorption	
45.00	79.72	22.1277
35.00	62.00	15.7307
30.00	53.15	13.2068
25.00	44.29	11.7117
15.00	26.57	7.5254
10.00	17.72	6.4347
5.00	8.86	5.3169
1.00	1.77	3.9252
10^{-6}	0.00	2.5690

order to completely remove the residual water from the adsorbent. Thus, if a lower regeneration temperature is used during the regeneration cycle in a temperature swing adsorption (TSA) operation, there will always be residual water left on the adsorbent.

Figures 7 and 8 provide an alternative representation of the equilibrium data in which the equilibrium loadings at all temperatures are plotted versus the relative humidity. Figure 7 has all the adsorption points while Figure 8 has all the desorption points. It is seen that the equilibrium loadings as a function of the relative humidity are essentially independent of temperature. The reason is that as the temperature increases at a fixed pressure, loadings decrease due to the exothermic nature of adsorption but relative humidities also decrease, due to the increase in the vapor pressure. The two effects are of comparable magnitude, and thus a plot of the equilibrium loading
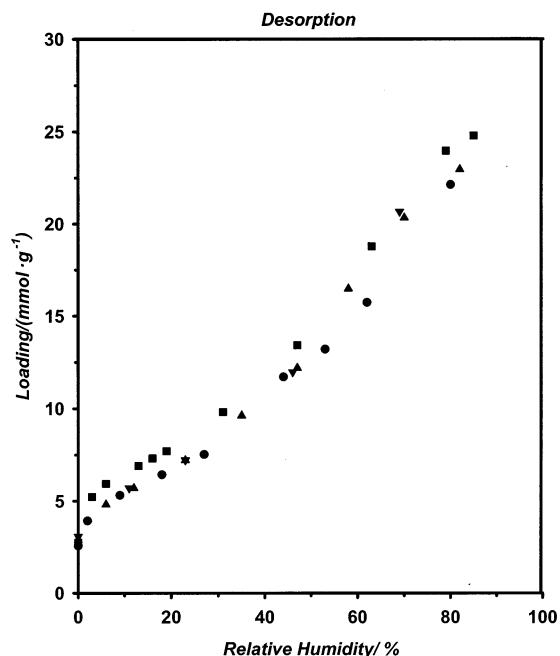
Figure 8. Equilibrium loading (desorption) versus relative humidity for water vapor on F-200 7 × 14 Tyler mesh activated alumina at multiple temperatures: ▼, $t = 5$ °C; ▲, $t = 15$ °C; ■, $t = 25$ °C; ●, $t = 35$ °C.

versus the relative humidity is almost independent of temperature. This is a convenient format to represent adsorption equilibrium data at multiple temperatures.[5,6]

Conclusions

Adsorption equilibrium isotherms of water vapor on F-200 7 × 14 commercially available activated alumina were measured at (5, 15, 25, and 35) °C using a static gravimetric technique. The isotherms were measured in the range 0% to approximately 95% relative humidity. The loading at 95% relative humidity was approximately 25 mmol/g. When plotted versus the relative humidity, the equilibrium loadings were essentially independent of temperature. A pronounced hysteresis between the adsorption and the desorption directions was present at all temperatures. Elevated temperature at vacuum conditions was needed in order to completely regenerate the adsorbent. The data reported in this study can be used not only in industrial design of drying units but also in the development of theoretical models for the adsorption/desorption mechanism of water vapor on activated alumina.

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