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Cosorption characteristics of solid adsorbents

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Abstract—Sorptive single-blow processes which adsorb simultaneously water vapor and carbon dioxide for applications in desiccant air-conditioning systems and indoor air quality control are documented. Cosorption processes are simulated for three different adsorbents, BPL activated carbon, silica gel (grade 40), and 13X molecular sieve. The process air stream is assumed to consist of binary mixture of water vapor and carbon dioxide, and the finite heat and mass transfer rates are assumed between air stream and surface of the adsorbent. The cosorption isotherms (equilibrium equations) of water vapor and carbon dioxide, correlated from available experimental data, are utilized to simulate the sorption processes. The dynamic cosorption performance of the three solid adsorbents exhibit widely different sorption characteristics, including the roll-over effect.

1. INTRODUCTION

SORPTIVE technologies have widespread applications. These include: dehydration of gases; solvent recovery from air leaving a chamber where an evaporative process occurs; odor removal and toxic gas removal in ventilation system or from vent gases for air pollution control; separation of rare gases (krypton, xenon) at low temperature, etc. In this study, we concentrate on the sorptive single-blow processes which are applied to dehydration of an airstream in desiccant air-conditioning systems and the potential of desiccant systems, through multicomponent cosorption, to improve indoor air quality.

According to the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) standard 62-1989, there are two acceptable procedures to control indoor air quality. One is called the "ventilation rate procedure" which provides ventilation air of a specified quality and quantity to achieve the acceptable indoor air quality. The other method is called the "indoor air quality procedure" which controls known and specifiable contaminants to achieve acceptable indoor air quality. The indoor air quality procedure provides a direct solution to the control of indoor contaminants by restricting the concentration of all known contaminants of concern to a specified acceptable level [1].

Absorption or adsorption processes can be utilized to remove the contaminants from indoor air. Absorption processes use liquid absorbents to remove pollutants from an airstream, while adsorption processes utilize solid adsorbents to remove pollutants from an airstream. In general, activated carbon, silica gel and molecular sieve are widely used in adsorption processes. In a study of a solid adsorbent, Majumdar and Worek [2] used a numerical method to predict the heat and mass transfer processes that occur during water vapor adsorption in a fixed bed including a gas-phase resistance to the surface of the adsorbent. Collier *et al.* [3] studied the factors which influence the efficiency and capacity of open-cycle adsorbent cooling systems. They investigated the influence of operating a system at four locations in the United States. Zheng and Worek [4] studied the heat and mass transfer processes in a rotary solid adsorbent dehumidifier using an implicit finite-difference scheme. They determined the optimal rotational speed using the outlet adsorption-side humidity profiles and the humidity wave fronts inside the adsorbent dehumidifier. Knight [5] used an analytical method to predict the low concentration of volatile organic compounds (VOCs) in a rotary activated carbon filter.

The above individual studies were concentrated on pure component adsorption processes. However, in practice, an airstream may contain multicomponent contaminants. Some of the contaminants interact each other during the adsorption processes, therefore resulting in a reduction in the adsorption capacities of certain adsorbents.

Mayer and Prausnitz [6] proposed a method called the ideal adsorbed solution theory which assumed the adsorbed mixture behaves as an ideal solution. Based on the ideal solution theory, one can calculate the multicomponent adsorption equilibrium from their pure component adsorption equilibrium. However, if the solutions are not ideal, this method is not valid. For example, the adsorption of a binary mixture of water vapor and carbon dioxide on molecular sieve bed cannot be predicted by this method. Ruthven [7] proposed a simplified statistical thermodynamic model to predict mixed-gas adsorption which took

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NOMENCLATURE

A	adsorption potential [J mol^{-1}]
A_m	mass transfer area [m^2]
$C_{w,R}$	reference specific heat of the matrix [kJ kg^{-1} K^{-1}]
C_i	inlet concentration [kg$_{adsorbate}$ kg$^{-1}_{dry\ air}$]
C_o	outlet concentration [kg$_{adsorbate}$ kg$^{-1}_{dry\ air}$]
$C_{p,a}$	specific heat of dry air [kJ kg^{-1} K^{-1}]
f	fraction of adsorbent in the matrix [kg$_{adsorbent}$ kg$^{-1}_{matrix}$]
h	heat transfer coefficient [W m^{-2} K^{-1}]
K_y	mass transfer coefficient [kg$_{adsorbate}$ m^{-2} s^{-1} kg$^{-1}_{adsorbate}$ kg$_{dry\ air}$]
K	Henry's constant
L	air passage length [m]
Le	overall Lewis number
m_w	mass of matrix [kg$_{matrix}$]
m	total dry air mass flow rate in process stream [kg$_{dry\ air}$ s^{-1}]
R	universal gas constant [J mol^{-1} K^{-1}]
t	adsorption time [s]
T	absolute temperature [K]
W_0	maximal adsorbate content [kg$_{adsorbate}$ kg$^{-1}_{adsorbent}$]
W_i	adsorbate content of i [kg$_{adsorbate}$ kg$^{-1}_{adsorbent}$]
x	axial coordinate in the air flow direction [m]
Y_i	mass fraction of the contaminant i in the air stream [kg$_{adsorbate}$ kg$^{-1}_{dry\ air}$]
$Y_{w,i}$	mass fraction of contaminant in equilibrium with adsorbents [kg$_{adsorbate}$ kg$^{-1}_{dry\ air}$].
Greek letters	
λ_1	non-dimensional parameter, equation (5)
λ_2	non-dimensional parameter, equation (6)
ξ	non-dimensional axial coordinate in the air flow direction
τ	non-dimensional time
ϕ	relative humidity.

into account the non-ideality caused by size differences of the adsorbed molecules. However, the method was specifically developed for the adsorption of zeolites. Kärger and Bülow [8] theoretically studied simultaneous adsorption of *n*-heptane and benzene on an NaX-zeolite. They discovered that the faster diffusion component, *n*-heptane, is adsorbed initially to a concentration level which exceeds the final equilibrium concentration.

In this study, we develop the governing equations to simulate simultaneous isothermal cosorption of two adsorbates and, using experimental equilibrium data developed by Hines and Ghosh [9], the cosorption processes on activated carbon, silica gel and molecular sieve are investigated. The experimental data developed by Hines and Ghosh [9] give adsorption data, for both a pure and a binary mixture of water vapor and carbon dioxide adsorbed on BPL activated carbon, silica gel (grade 40), and molecular sieve 13X. Due to the limitation of the experimental data, the equilibrium equations for carbon dioxide are assumed to be linear, and those of water vapor are characterized by the Dubinin–Polanyi equation. The results of the correlated equilibrium equations are within 5% compared to the given experimental data.

2. GOVERNING AND EQUILIBRIUM EQUATIONS

In this study, the following assumptions are made to simulate the combined heat and mass transfer processes that occur in an adsorber: (1) uniform and constant concentration at the inlet to the matrix; (2) constant specific heats per unit mass for the fluid and the desiccant; (3) constant air velocities and pressure; (4) equal mass and heat transfer areas; (5) finite and constant mass and heat transfer coefficients; (6) the matrix consists entirely of desiccant with no supporting material in the matrix; (7) number of transfer units (NTU) for heat transfer is equal to 15; (8) overall Lewis number is equal to 1.0; and (9) the adsorbent matrix consists of parallel passages.

According to the assumption (9), since the air passages in the matrix are modeled as parallel, we take the control volume of length dx as shown in Fig. 1, and apply the conservation of mass for each adsorbate: thus we obtain

$$\left(f\frac{m_w}{L}\right)\frac{\partial W_i}{\partial t}+\dot{m}\frac{\partial Y_i}{\partial x}=0. \tag{1}$$

The contaminants transport equation between the airstream and the adsorbent can be written as

$$(fm_w)\frac{\partial W_i}{\partial t}=K_y\,(A_m)\,(Y_i-Y_{w,i}). \tag{2}$$

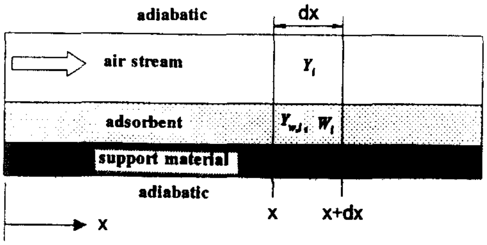

FIG. 1. Processing air stream channel and control volume of mass transfer.

Substituting equation (2) into equation (1), we obtain

$$(\dot{m}L)\frac{\partial Y_i}{\partial x} = K_y(A_m)\,(Y_{w,i} - Y_i)\,. \tag{3}$$

In order to obtain the non-dimensional governing equations, we introduce the following non-dimensional parameters:

$$\zeta = \frac{hA_m x}{\dot{m}C_{p,a}L} = NTU\left(\frac{x}{L}\right), \tag{4}$$

$$\lambda_1 = \frac{K_y C_{p,a}}{h} = \frac{1}{Le}, \tag{5}$$

$$\lambda_2 = \left(\frac{K_y}{h}\right)\left(\frac{C_{w,R}}{f}\right) = \frac{C_{w,R}}{Le\,C_{p,a}f}, \tag{6}$$

$$\tau = \frac{hA_m t}{m_w C_{w,R}}. \tag{7}$$

In this study, we assumed $Le = 1.0$, $C_{p,a} = 1.0$ kJ kg^{-1} K^{-1}, $C_{w,R} = 1.0$ kJ kg^{-1} K^{-1}, and, according to assumption 6, $f = 1.0$. Hence equations (2) and (3) become

$$\frac{\partial Y_i}{\partial \zeta} = (Y_{w,i} - Y_i), \tag{8}$$

$$\frac{\partial W_i}{\partial \tau} = (Y_i - Y_{w,i}). \tag{9}$$

In this work, we investigate the breakthrough characteristics of different adsorbent materials. Therefore, we assume the sorbent is fully regenerated and the inlet conditions are constant. This gives the following initial and boundary conditions:

$$W_i = 0 \quad \text{at}\ \tau = 0\,, \tag{10}$$

$$Y_i = Y_{\text{inlet},i} = \text{constant} \quad \text{at}\ \zeta = 0\,. \tag{11}$$

In equations (8) and (9), there are three unknowns; therefore, a third equation is needed which is the equilibrium sorption characteristic which relates the adsorbate uptake to equation. In this study, we correlated the experimental data of Hines and Ghosh [9] to obtain the equilibrium relations for water vapor and carbon dioxide adsorption data on activated carbon, silica gel and molecular sieve at 298 K.

2.1. *Water vapor adsorption on activated carbon, silica gel, and molecular sieve in the presence of carbon dioxide*

For water vapor (both pure component and binary mixture), the Dubinin–Polanyi equation is valid for these three adsorbents. Applying the Dubinin–Polanyi equation, we define the adsorption potential, A as

$$A = -RT\ln(\phi)\,, \tag{12}$$

where R is the universal gas constant (J mol^{-1} K^{-1}), T is the temperature (K) and ϕ is the relative humidity. In order to correlate the equilibrium equation within the experimental error [10], the water vapor adsorbed on activated carbon for pure component and binary mixture, the Dubinin–Polanyi equation is modified to

$$W_{H_2O} = W_0\exp\left[-\left(\frac{A}{E_1}\right)+\left(\frac{A}{E_2}\right)^2\right],$$

$$0.21 \leqslant \phi \leqslant 0.65\,, \tag{13}$$

where E_1 and E_2 are the correlated coefficients which at low loadings are assumed to be linearly dependent on the concentration of carbon dioxide as expressed in equations (14) and (15):

$$E_1 = a_1 - b_1 Y_{CO_2}\,, \tag{14}$$

$$E_2 = a_2 - b_2 Y_{CO_2}\,, \tag{15}$$

where Y_{CO_2} is the mass fraction of carbon dioxide in kg kg^{-1}, and the values of W_0, a_1, a_2, b_1, and b_2 are listed in Table 1. For $\phi < 0.21$, we assume a linear relationship:

$$W_{H_2O} = K\phi \quad \phi < 0.21\,, \tag{16}$$

where K is Henry's constant. For pure water vapor and for binary mixture of water vapor and carbon dioxide adsorption, we determined $K = 0.02324$.

For binary adsorption of water vapor on silica gel and molecular sieve the original Dubinin–Polanyi equation is valid:

$$W_{H_2O} = W_0\exp\left[-\left(\frac{A}{E_2}\right)^2\right] \quad 0 \leqslant \phi \leqslant 0.65\,, \tag{17}$$

where E_2 is expressed in equation (15), and correlated coefficients W_0, a_2 and b_2 also are listed in Table 1.

2.2. *Carbon dioxide adsorption on activated carbon, silica gel, and molecular sieve*

2.2.1. *Pure component.* Due to the limitations of the experimental data, the equilibrium equations for carbon dioxide on these three adsorbents are again assumed to be linearly dependent on the concentration, for concentrations between 0 and 1100 ppm. Hence, for pure carbon dioxide on activated carbon, silica gel and molecular sieve, the equilibrium equation is given by

$$W_{CO_2} = KY_{CO_2}\,, \tag{18}$$

where the values of Henry's constant K are listed in Table 2.

2.2.2. *Binary adsorption of water vapor and carbon dioxide.* Taking into effect the presence of water vapor on the adsorption of carbon dioxide by activated carbon, silica gel and molecular sieve, the equilibrium equation can be expressed as

$$W_{CO_2} = \frac{1+B_2\phi+B_4\phi^2+B_6\phi^3}{B_1+B_3\phi+B_5\phi^2}Y_{CO_2}, \tag{19}$$

where the coefficients, B_1–B_6, for activated carbon, silica gel and molecular sieve are given in Table 3. The correlated error of the above equilibrium equations

Table 1. The correlated coefficients for water vapor on the adsorbents at 298 K

Adsorbents	W_0 (g g^{-1})	a_1 (J mol^{-1})	b_1 (J mol^{-1} g g^{-1})	a_2 (J mol^{-1})	b_2 (J mol^{-1} g g^{-1})
Activated carbon	8.1457	262.3526	1251.2154	1426.1047	6402.4627
Silica gel	0.3564	N/A	N/A	3916.8738	68 476.129
Molecular sieve	0.2506	N/A	N/A	6782.9239	250 000.0

Table 2. The correlated coefficients of Henry's constant K for pure adsorption of carbon dioxide on the adsorbents at 298 K

Adsorbents	K
Activated carbon	0.1255
Silica gel	0.1196
Molecular sieve	9.5650

are within 5% for given experimental data which are certainly within the reported experimental error [10]. Figures 2 and 3 show the adsorption isotherms on these three adsorbents according to the results of equations (12)–(19) and experimental data.

Figures 4(b), 5(c) and 6(b) show the adsorption capacities of the water vapor and carbon dioxide on activated carbon, silica gel, and molecular sieve, respectively. From Fig. 4(b), as a result of the cosorption of water vapor and carbon dioxide, the adsorption capacities of water vapor on activated carbon decrease by less than 4% relative to its pure component adsorption, while the adsorption capacities of carbon dioxide decreased by more than 35% relative to its pure component capacity. Figure 5(c) shows that the adsorption capacities of water vapor on silica gel decreased by approximately 5% relative its pure component capacities, while the capacities of carbon dioxide decreased by approximately 59%. Figure 6(b) shows that the adsorption capacities of water vapor on molecular sieve decreased by 10% relative to its pure component capacities, while the capacities of carbon dioxide decreased by approximately 75%.

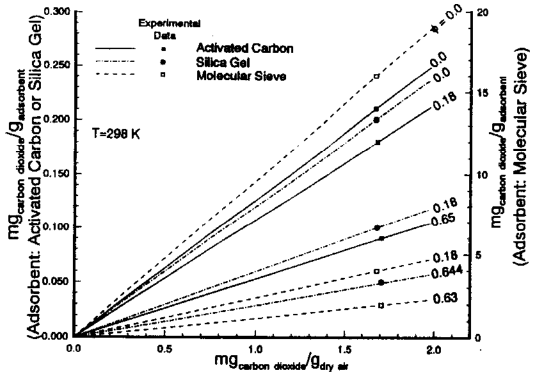

FIG. 2. Equilibrium adsorption isotherms of carbon dioxide on activated carbon, silica gel, and molecular sieve at 298 K.

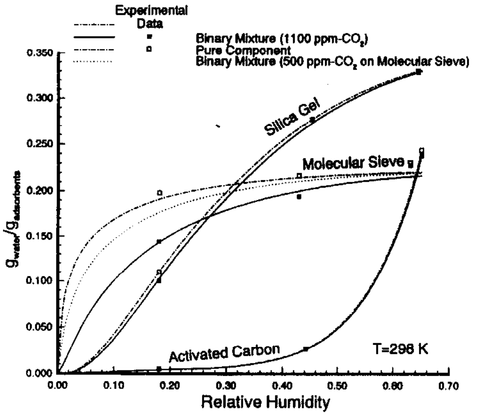

FIG. 3. Equilibrium adsorption isotherms of water vapor on various adsorbents.

3. NUMERICAL SOLUTION TECHNIQUE

The governing equations, equations (8) and (9), the initial condition given by equation (10), the boundary condition of equation (11) and equilibrium equations given by equations (12)–(19) are solved by an explicit finite-difference method with uniform spatial step ($\Delta\zeta$) and non-uniform time step ($\Delta\tau$).

First of all, equation (8) is solved at initial time and then equation (9) is solved by using the values of Y_i which are computed from equation (8). With the calculation proceeding, we assumed quasi-equilibrium in each spatial step. At the quasi-equilibrium condition, the inversions of equations (12)–(19) are applied to obtain the values of $Y_{w,i}$. It should be noted

Table 3. The correlated coefficients for the variations of water vapor on Henry's constant K for carbon dioxide on the adsorbents at 298 K

Adsorbents	B_1	B_2	B_3	B_4	B_5	B_6
Activated carbon	7.9655	−4.9891	−35.4151	9.9013	64.958	−4.6871
Silica gel	8.3638	−5.0900	−4.8400	16.415	44.777	−14.397
Molecular sieve	0.10454	−9.3526	−0.36047	38.2398	3.2828	−35.710

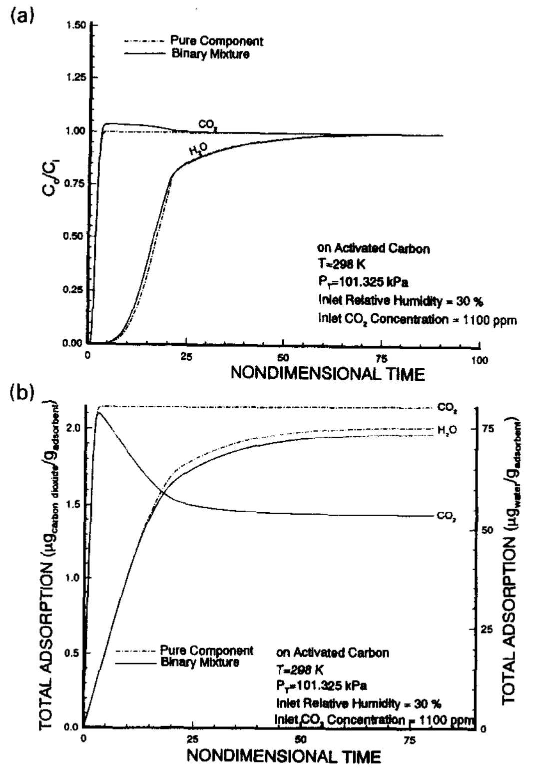

FIG. 4. (a) Breakthrough curves for carbon dioxide and water vapor in an activated carbon bed at 298 K. (b) Adsorption capacities of water vapor and carbon dioxide on an activated carbon bed for pure component and binary mixture at 298 K.

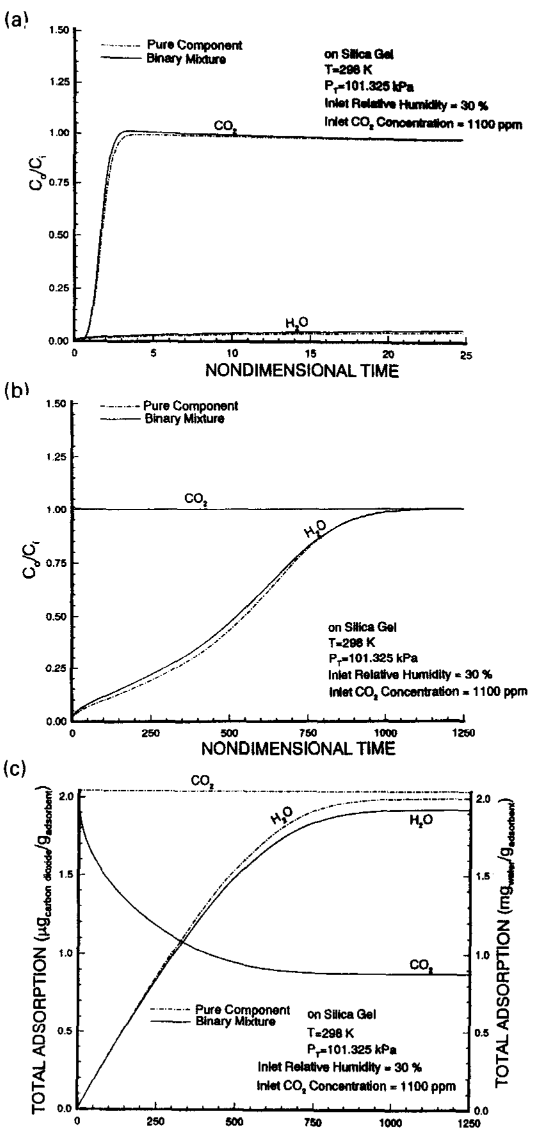

FIG. 5. (a) Breakthrough curves for carbon dioxide and water vapor in a silica gel bed at 298 K. (b) Breakthrough curves for carbon dioxide and water vapor in a silica gel bed at 298 K. (c) Adsorption capacities of water vapor and carbon dioxide in a silica gel bed for pure component and binary mixture at 298 K.

that at quasi-equilibrium condition the values of Y_i in equilibrium equations, equations (12)–(19), are equal to $Y_{w,i}$.

In order for the numerical approach to be convergent and stable, we determined that $\Delta\tau \leqslant 0.15$ and $\Delta\zeta \leqslant 0.15$. This gives results that vary within 2.0×10^{-4}% for water vapor sorption and 8.0×10^{-4}% for carbon dioxide sorption on activated carbon. For silica gel we determined that $\Delta\tau \leqslant 0.09$ and $\Delta\zeta \leqslant 0.25$. This gives results that vary within 1.5×10^{-3}% for water vapor and 6.0×10^{-3}% for carbon dioxide. Finally for molecular sieve $\Delta\tau \leqslant 0.4$ and $\Delta\zeta \leqslant 0.25$ gives results that vary within less than 3.0×10^{-4}% for water vapor sorption and 6.0×10^{-4}% for carbon dioxide sorption.

4. RESULTS AND DISCUSSION

Numerical solutions of the governing equations were obtained for the case of a single-blow sorption process with the process being isothermal at 298 K and maintaining the total pressure at 101.325 kPa. The inlet relative humidity was maintained at 30%, and inlet concentration of carbon dioxide was at 1100 ppm. The governing equations, equations (8) and (9), are the same for the sorption process on activated carbon, silica gel, and molecular sieve for both pure component and binary mixture adsorption. The only differences between these adsorbents are the utilization of the different equilibrium equations. As expected, carbon dioxide takes a shorter time to achieve equilibrium for both pure and binary mixture conditions. Figures 4(a), 5(a) and (b), and 6(a) show the breakthrough curves on activated carbon, silica gel, and molecular sieve, respectively. From these results, we find that carbon dioxide diffusion is faster than that of water vapor and the adsorbents have a stronger affinity for water vapor. Carbon dioxide initially is adsorbed very rapidly. However, when the water vapor begins to be adsorbed by the adsorbent the carbon dioxide is displaced, which causes the outlet carbon dioxide concentration to exceed the inlet

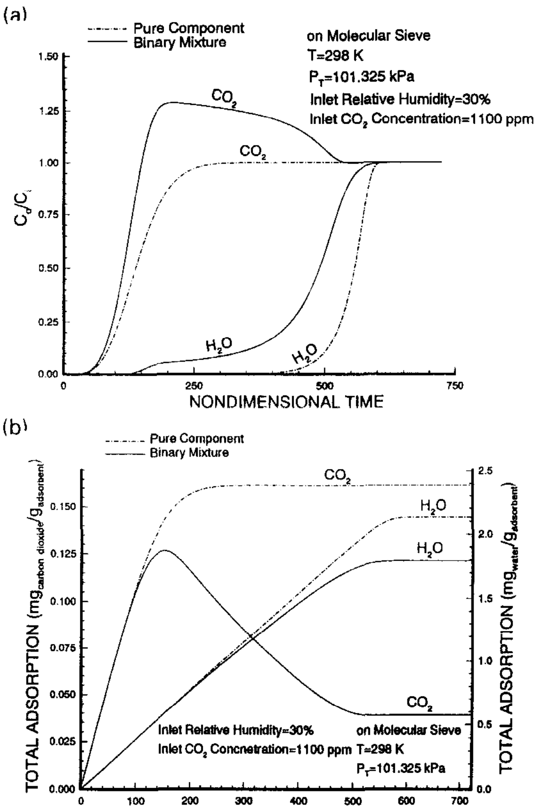

FIG. 6. (a) Breakthrough curves for water vapor and carbon dioxide in a molecular sieve bed at 298 K. (b) Adsorption capacities of water vapor and carbon dioxide in a molecular sieve bed for pure component and binary mixture at 298 K.

concentration. This is called the roll-over effect [11]. The roll-over effect is more pronounced for the sorption process on molecular sieve than on activated carbon or silica gel.

We apply the ideal adsorbed solution theory proposed by Mayer and Prausnitz [6] to calculate the cosorption uptake of water vapor and carbon dioxide. As expected, the ideal adsorbed solution theory is not valid for the binary mixture adsorption of water vapor and carbon dioxide on activated carbon, silica gel and molecular sieve. It is probably due to water vapor and carbon dioxide not being from the same chemical group, and these two components interacting with each other during adsorption.

The equilibrium equations proposed in this study are only valid at a temperature equal to 298 K. For a wider range of temperature, the correlated coefficients listed in Table 1 should be modified by introducing more experimental data at various temperatures, and the correlated coefficients listed in Tables 2 and 3 should be expressed in terms of temperature.

The linear relationship in the adsorption isotherm assumes that the carbon dioxide on activated carbon and silica gel is more accurate than on molecular sieve. For carbon dioxide on BPL activated carbon in the temperature range of 212.7–323 K, the equilibrium equation deviates from the linear relationship when the carbon dioxide concentration is higher than 1400–10 000 ppm. However, for carbon dioxide on silica gel and 13X molecular sieve in the temperature range of 298–323 K, the equilibrium equation deviates from the linear relationship when the carbon dioxide concentration is more than 650–800 ppm [12]. For carbon dioxide on silica gel TK800, *E*, and *J* for the temperature range of 298–1273 K, the equilibrium equation deviates from the linear relationship when the carbon dioxide concentration is larger than 12 000–40 000 ppm [13].

5. CONCLUSIONS

The cosorption isothermal dynamic behaviors on activated carbon, silica gel, and molecular sieve are presented. The simultaneous presence of water vapor and carbon dioxide in process air decreases the adsorption capacities on these three adsorbents. The roll-over effect, which occurs when the outlet concentration is higher than the inlet concentration, appears in the breakthrough curves of carbon dioxide. This effect is due to faster diffusion and a lower affinity of carbon dioxide than water vapor for the adsorbents. This effect is more pronounced for the cosorption process on molecular sieve than on activated carbon and silica gel.

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