

CLOSE AND OPEN CYCLE ADSORPTION KINETICS: DEVELOPMENT OF CORRELATION FOR DESICCANT AIR-CONDITIONING

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ABSTRACT

Adsorption kinetics by desiccant-water pairs always play curial role in the development of low-cost thermally driven desiccant air-conditioning systems. It also influences various operating parameters of desiccant air-conditioning systems e.g. switching/cycle time, desiccant/system size, and regeneration temperature etc. Usually it is difficult to measure open-cycle adsorption kinetics precisely in adsorption heat pump systems. Therefore, present study provides an experimental comparison of close and open cycle based water vapor adsorption kinetics for the development of desiccant air-conditioning system. In this regard, a polymer based hydrophilic sorbent was used for close and open cycle adsorption measurements. Gravimetric method based magnetic suspension adsorption measurement unit was used for close-cycle adsorption kinetics measurements. However, the open-cycle adsorption kinetics was determined from the instantaneous measurement of air relative humidity and dry-bulb temperature in and out to the desiccant block while assuming the equilibrium between air and desiccant sides. Both experimental results were analyzed using linear driving force (LDF) model which presents the best regression of the experimental data. Furthermore, an empirical correlation of close to open cycle water vapor adsorption kinetics was established. Results revealed that the open-cycle kinetics of water vapor adsorption was 0.65 times slower (on average) than the close-cycle, which was more likely due to the complex mechanism of adsorption kinetics in open system. This study can be useful to determine the open-cycle adsorption kinetics from the close system data for designing the desiccant air-conditioning system.

KEYWORDS: adsorption kinetics, water vapor, polymer, open-cycle, close-cycle

Nomenclature

t time [s]

\bar{D}_s open-cycle surface diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]

T temperature [$^{\circ}\text{C}$ or K]

D_s close-cycle surface diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]

$W(0)$ initially adsorbed water vapors [$\text{kg}_w \text{kg}_{\text{ads}}^{-1}$]

D_s/R_p^2 close-cycle diffusion time constant [s^{-1}]

$W(t)$ or w instantaneous adsorption uptake [$\text{kg}_w \text{kg}_{\text{ads}}^{-1}$]

\bar{D}_s/R_p^2 open-cycle diffusion time constant [s^{-1}]

W or $W(\infty)$ equilibrium adsorption uptake [$\text{kg}_w \text{kg}_{\text{ads}}^{-1}$]

$\partial w/\partial t$ adsorption or desorption rate [$\text{kg}_w \text{kg}_{\text{ads}}^{-1} \text{s}^{-1}$]

γ close to open cycle correlation factor [-]

F_o geometric parameter for adsorbent particle [-]

Subscripts

HR humidity ratio [$\text{kg}_w \text{kg}_{\text{DA}}^{-1}$]

ads adsorption

M adsorbent/desiccant mass [kg_{ads}]

eva evaporator

\dot{m} mass flow rate [$\text{kg} \text{s}^{-1}$]

in inlet to desiccant

R_p radius of the sorbent particle [m]

out outlet to desiccant

RH relative humidity [%]

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INTRODUCTION

Water vapor adsorption has been extensively studied for the development of close and open cycle based adsorption heat pump systems particularly desiccant air-conditioning (AC) systems¹⁻³. A simplified schematic diagram of desiccant AC system is presented in Figure 1. In this regard, volumetric and gravimetric methods are commonly used for the measurement of instantaneous and equilibrium adsorption uptakes⁴⁻⁷. For both methods, the equilibrium adsorption amount is somehow comparable in the close and open systems. However, the instantaneous adsorption uptake at atmospheric conditions could be entirely different due to the complex adsorption kinetics mechanism. It is relatively difficult to measure the water vapor adsorption kinetics in open system specially when dealing with small amount of adsorbents. Mostly open-cycle water vapor sorption is studied in food and agriculture sector using saturated salt solution technique^{8,9}. On the other hand it can be measured by close system with high accuracy. Therefore, present study experimentally investigated the close and open cycle water vapor adsorption kinetics and developed an empirical correlation for the conversion of close-cycle kinetics into open-cycle kinetics. A typical polymer based hydrophilic sorbent (TPBS) in the form of desiccant block was used for both types of experiments¹⁰⁻¹⁴. The desiccant blocks were provided by Showa Manufacturing Co., Ltd. Japan.

EXPERIMENTAL SECTION

Close-cycle experiment

Close-cycle kinetics of water vapor adsorption on TPBS has been measured gravimetrically using magnetic suspension adsorption measurement unit⁴. The simple representation of the experimental unit is given in Figure 2. The experimental unit consisted of: (1) an adsorption measurement unit based on magnetic suspension technology, (2) blend of low, medium and high capacity vacuum pumps, (3) constant temperature oil circulators, (4) a digital data logger which systematically records the experimental data, (5) a thermally controlled evaporator, and (6) constant temperature air circulator in order to avoid condensation. The adsorption amount was measured gravimetrically in the magnetic suspension technology with no contact with the adsorbent cell. The key components of the magnetic balance are electronic

control unit, stable magnet, and sensor code. The unit introduces electronic signals which keep the adsorbent in suspension. The signal strength was translated into the actual water vapor adsorption amount at later stage.

The uncertainty in the measurement of adsorption amount was thirty micrograms in maximum whereas the corresponding relative error does not exceeds more that 0.002%. The experimental unit enables three pressure measuring gauges as shown in Figure 2 that can measure the entire range of vapor pressure. The uncertainties in the measurement of pressure gauges were ranging from 15E-2 to 25E-2 percent of the full scale. Using the experimental accessories, the water vapor adsorption was recorded on PC by means of digital data logger.

Nearly 200 mg of TPBS was used for water vapor adsorption measurements. In the beginning the sample regeneration was made on more than 120°C for 3 to 5 hours at vacuum pressure of 3E-5 Pa. Later the refrigerant and adsorbent temperatures were carried to the first measuring point of the adsorption isotherm. The valves were opened for adsorption once the steady-state condition of temperature arises on both sides. Consequently, the instantaneous water vapor adsorption data were obtained for all the measuring points of adsorption isotherm. Multistep technique^{4,5} of sorption measurement was employed in the current study by which the water vapor adsorption isotherms are obtained at 22°C to 24°C. On the other hand, refrigerant temperature was ranging from 1°C (at minimum) to adsorption cell temperature (at maximum). However, the maximum relative pressure was always less than to 0.90 in all experiments.

Open-cycle experiment

Open-cycle kinetics of water vapor adsorption on TPBS were measured using an experimental apparatus based on instantaneous measurement of air relative humidity (RH) and dry-bulb temperature. The schematics diagram of the experimental apparatus is shown in Figure 3. The system consisted of TPBS made honeycomb like eight desiccant blocks; humidity and temperature sensors (Vaissala HMT330); fans to regulate the flow rate by changing the pressure difference; an orifice structure for flow measurement; two units for the control of temperature and RH of process and regeneration air flows (Apiste: PAU-A1400S-HC & PAU-AZ1800SE) for

moisture adsorption and desorption on the TPBS; flow control gates for switching the air flows; and a data logger for systematic recording of data into PC.

Firstly, water vapors desorption from the desiccant block was conducted by passing the regeneration air of 50°C and RH less than 10% for two hours in order to achieve the initial conditions for air dehumidification or adsorption process. The system was switched from regeneration air to process air flow once the equilibrium condition of temperature and humidity was obtained. The process air temperature ranged from 21.2°C to 23.1°C. The flow rate was kept constant (0.10 kg s⁻¹) for both process and regeneration air flows. Numerous experiments with variable conditions were conducted and process and regeneration air flows were passed from the desiccant blocks in a systematic way. Consequently, the instantaneous change in temperature and RH on each side of desiccant block was recorded.

DATA REDUCTION

Close-cycle experiment

The instantaneous water vapor adsorption data of TPBS obtained from the close-cycle experimental unit was analyzed by well-known linear driving force (LDF) model^{15, 16}. It is one of the commonly used model in simulating the kinetics of the adsorption process by which the adsorption rate (dw/dt) of the adsorbent/adsorbate pairs can be estimated with the following relationship^{15, 16}:

$$\left(\frac{dw}{dt}\right) = \frac{F_o D_s}{R_p^2} (W - w) \quad (1)$$

where W and w represent the equilibrium and instantaneous adsorption uptakes [kg kg⁻¹], respectively. F_o is a geometric parameter for adsorbent particle shape and it is equal to 15 for spherical adsorbent particle. The parameters D_s and R_p are the close-cycle surface diffusion coefficient [m² s⁻¹] and radius of the adsorbent particle [m], respectively. By integrating the Eq. (1) one can obtain the fractional uptake, F as a function of dimensionless time, θ¹⁶.

$$F = 1 - \exp(-F_o \theta) \quad (2)$$

where the fractional uptake and dimensionless time can be further translated as:

$$F = \frac{W(t) - W_0}{W_\infty - W_0} \quad (3)$$

$$\theta = \frac{D_s}{R_p^2} t \quad (4)$$

The parameters are explained in nomenclature. The linearization of the Eq. (2) gives the following form:

$$\ln(1-F) = -F_o \theta = -F_o \frac{D_s}{R_p^2} t \quad (5)$$

Plot of ln(1-F) versus adsorption time will yield a straight line with slope of $(-F_o D_s / R_p^2)$ and intercept equals zero.

Open-cycle experiment

The open-cycle experimental data was obtained in terms of RH and dry-bulb temperature in and out from the desiccant block. Assuming equilibrium between air and adsorbent sides, the instantaneous water vapor adsorption uptake by the TPBS, w [kg_w kg_{ads}⁻¹] was determined by Eq. (6) as follows:

$$w = W(0) + \frac{\dot{m}}{M} (HR_{in} - HR_{out}) \quad (6)$$

where \dot{m} and M represent air mass flow rate [kg_{DA} s⁻¹] and dry mass of TPBS [kg_{ads}], respectively. The parameters W(0) and HR denote initially adsorbed water vapors at time equals zero [kg_w kg_{ads}⁻¹] and air humidity ratio [kg_w kg_{DA}⁻¹], respectively. The subscript in and out stands for inlet and outlet to the desiccant block, respectively. For the process air flow, (HR_{in} - HR_{out}) is positive which indicates the water vapor adsorption on the TPBS, whereas it is opposite in case of regeneration air flow.

Consequently the instantaneous water vapor adsorption data were analyzed by the LDF model in the following form:

$$\left(\frac{dw}{dt}\right) = \frac{F_o \bar{D}_s}{R_p^2} (W - w) \quad (7)$$

The bar (̄) sign represent the parameter based on open-cycle system. Therefore, \bar{D}_s represents the open-cycle surface diffusion coefficient [m² s⁻¹]. Rests of the parameters have same meaning for close and open cycle systems.

Eq. (7) can be integrated for open-cycle fractional

uptake. Consequently, the linearization of the resulted equation can be as follows:

$$\ln(1 - \bar{F}) = -F_o \frac{\bar{D}_s}{R_p^2} t \quad (8)$$

A plot of $\ln(1 - \bar{F})$ versus time will be required in order to determine the open-cycle surface diffusion coefficient, \bar{D}_s from the slope.

Close to open cycle kinetics correlation

An empirical correlation (ζ) for close to open cycle adsorption kinetics was established by dividing the adsorption kinetics equation of LDF model for open and close cycles as given below:

$$\zeta = \frac{\text{Open-cycle LDF model}}{\text{Close-cycle LDF model}} = \frac{\text{Eq. (7) or Eq. (8)}}{\text{Eq. (1) or Eq. (5)}} \quad (9)$$

$$\zeta = \frac{\ln(1 - \bar{F})}{\ln(1 - F)} = \left(-F_o \frac{\bar{D}_s}{R_p^2} t \right) / \left(-F_o \frac{D_s}{R_p^2} t \right) = \frac{\bar{D}_s}{D_s} \quad (10)$$

$$\bar{D}_s = D_s \zeta \quad (11)$$

In principle, value of ζ should be less than unity because of complex mechanism of adsorption kinetics and competitive effect of other gasses present in the air. The term $\zeta=1$ indicates that the TPBS will adsorb the water vapor from the air with an identical rate as it adsorb in the close system under vacuum conditions. In other words, the presented correlation is also an alternative or indirect technique to analyze the fact of competitive effect by the gasses present in the air.

RESULTS AND DISCUSSION

Kinetics of water vapor adsorption onto TPBS were measured at 22°C to 24°C using close-cycle based magnetic suspension adsorption measurement unit as shown in Figure 2. The experimental data were analyzed with well-known LDF model. Due to the simplicity and consistency, the model has been extensively studied in order to represent the adsorption kinetics for many adsorbent/refrigerant pairs^{17,18}. The applicability of LDF model depends on linear plot of versus adsorption time. Figure 4(a) and (b) shows the fitting results of LDF model with the experimental data obtained from close-cycle system. Results reported that LDF model gave the precise regression of experimental data at various pressures. Hence, all experimental points were analyzed using the LDF model.

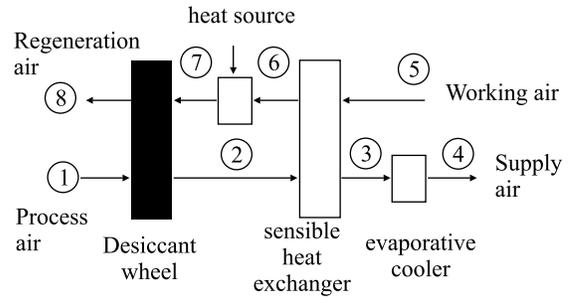


Figure 1. Schematic diagram of the conventional desiccant air-conditioning system.

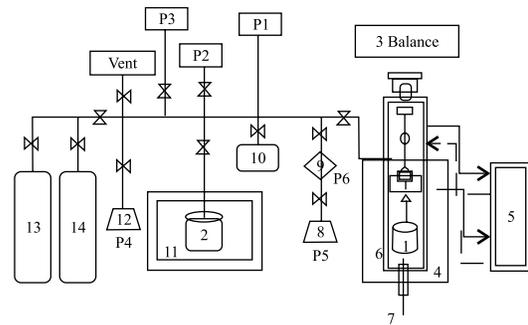


Figure 2. Schematic diagram of the close-cycle based magnetic suspension adsorption measurement unit: (1) adsorbent, (2) refrigerant, (3) magnetic suspension balance, (4) oil circulation jacket, (5) isothermal oil bath, (6) high speed heater (regeneration), (7) thermocouples, (8) rotary pump, (9) turbo-molecular pump, (10) buffer, (11) isothermal oil bath, (12) diaphragm pump, (13) nitrogen gas, (14) helium gas, and (P1 to P6) pressure gauges.

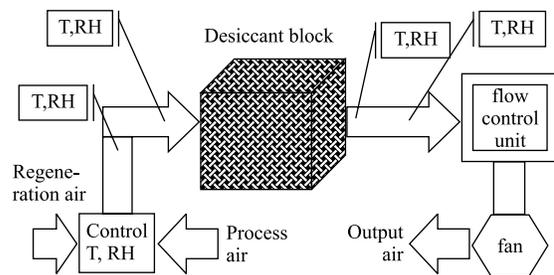


Figure 3. Schematic diagram of the open-cycle based experimental apparatus.

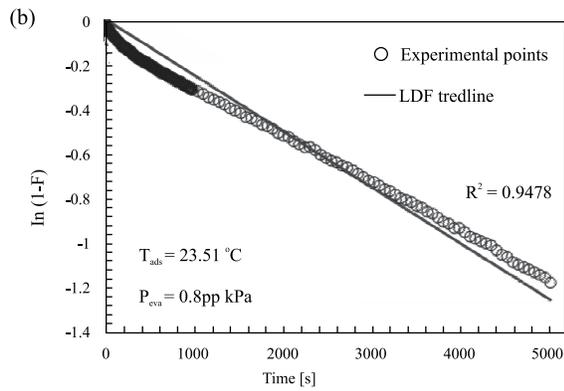
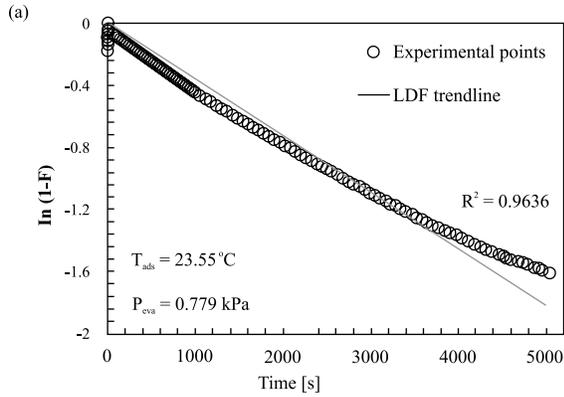


Figure 4. Linear plots of $\ln(1-F)$ versus adsorption time for close-cycle water vapor adsorption measurement at: (a) $T_{ads} = 23.55^\circ\text{C}$ & $P_{eva} = 0.779\text{kPa}$; and (b) $T_{ads} = 23.51^\circ\text{C}$ & $P_{eva} = 0.899\text{ kPa}$.

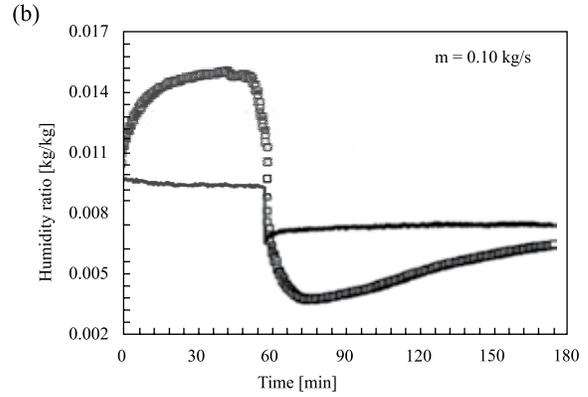
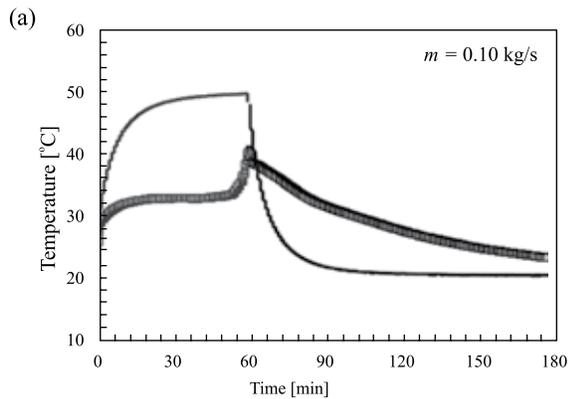


Figure 5. Open-cycle experimental result profiles for: (a) temperature; and (b) humidity ratio. Lines and points represent inlet and outlet conditions to the desiccant, respectively. Red and blue colors are used for regeneration and process air flows, respectively.

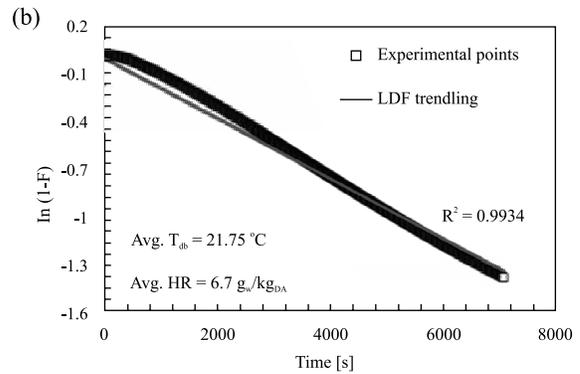
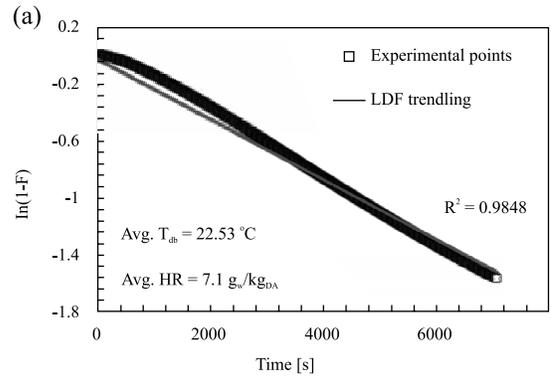


Figure 6. Linear plots of $\ln(1-F)$ versus adsorption time for adsorption phase of two open-cycle experiments at inlet air conditions of: (a) $T_{db} = 22.53^\circ\text{C}$ & $\text{HR} = 7.1\text{ gw/kgDA-1}$; and (b) $T_{db} = 21.75^\circ\text{C}$ & $\text{HR} = 6.7\text{ gw/kgDA-1}$.

Table 1. Fitting results of LDF model for close and open cycle experimental data.

Open-cycle adsorption kinetics			Close-cycle adsorption kinetics			ζ [-]
Avg. Tads	$F_o \frac{\overline{D_s}}{R_p^2}$	Avg. $F_o \frac{\overline{D_s}}{R_p^2}$	Avg. Tads	$F_o \frac{D_s}{R_p^2}$	Avg. $F_o \frac{D_s}{R_p^2}$	
23.09	2.51E-04	1.90E-04	23.55	3.26E-04	2.92E-04	0.65
23.07	2.47E-04		23.51	2.23E-04		
22.60	2.36E-04		23.52	2.51E-04		
22.53	2.36E-04		22.00	2.33E-04		
21.75	2.06E-04		22.00	1.31E-04		
21.15	1.17E-04		22.01	5.89E-04		
20.97	1.29E-04					
21.55	1.40E-04					
21.21	1.50E-04					

Consequently, close-cycle surface diffusion coefficient D_s values were determined from the slope of the plots for various experimental conditions. Optimized results for estimation of close-cycle surface diffusion coefficient are presented in Table 1.

In case of open-cycle experiments, instantaneous variation of desiccant inlet/outlet RH and dry-bulb temperatures were determined using open-cycle based experimental apparatus. Figure 5(a) and (b) showed the typical experimental results from the open-cycle experimental unit for dry-bulb temperature and humidity ratio, respectively. Assuming the equilibrium between air and adsorbent sides, the instantaneous water vapor adsorption uptake was determined by Eq. (6).

Open-cycle data of instantaneous adsorption uptake obtained using Eq. (6) was analyzed by LDF model. The model successfully represents the data for various experimental conditions. Figure 6(a) and (b) presents the plot of $\ln(1-\bar{F})$ versus adsorption time for two experimental conditions. Results revealed that the model gave the precise fit of the experimental data with coefficient of determination equals 0.98 to 0.99. All the experiments were analyzed for various experimental conditions using the LDF model. Consequently, the open-cycle surface diffusion coefficient $\overline{D_s}$ values were determined from the slope of the plots. The estimated values $\overline{D_s}$ are furnished in Table 1.

Finally, the close to open cycle correlation (ζ) for water

vapor adsorption kinetics of TPBS was determined using Eq. (11). Average value of close to open cycle kinetics correlation ζ was found 0.65 as presented in Table 1. It means that open-cycle kinetics of water vapor adsorption on TPBS was 0.65 times slower than the close-cycle. Complex mechanism of adsorption kinetics in open system and competitive effect of other gasses present in the air are might be the reasons of this kind of behavior.

CONCLUSIONS

Present study experimentally determined the close and open cycle kinetics of water vapor adsorption on a polymer based hydrophilic sorbent. In this regard, two experimental apparatus based on close and open cycle system were employed. The instantaneous water vapor adsorption data were analyzed by LDF model. The LDF model presented the best regression of the experimental data under various experimental conditions. Furthermore, an empirical correlation of close to open cycle water vapor adsorption kinetics was established. Results reported that the close to open cycle kinetics correlation ζ was found to be 0.65. These finding revealed that open-cycle kinetics of water vapor adsorption on polymer sorbent was 0.65 times slower than the close-cycle. It is due to the complex mechanism of adsorption kinetics at atmospheric conditions as well as competitive effect of other gasses present in the air. Results of this study can be useful to determine open-cycle adsorption kinetics from the close system data for designing the desiccant air-conditioning system.

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