Adsorption (2006) 12:167–174
DOI 10.1007/s10450-006-0143-2

Removal of heat of adsorption from adsorbent by forced convection

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Received: 4 January 2006 / Revised: 26 July 2006 / Accepted: 5 September 2006

Abstract An analytical mathematical model is used to investigate the effectiveness of forced convection for removal of the heat of adsorption from an adsorbent mass undergoing a differential adsorption process in a flow system. An example of such a process is measurement of gas adsorption kinetics using a differential adsorption bed. Isothermal operation may not be achieved even when a high gas flow rate is used, particularly if the sorption kinetics is relatively fast. Very small changes in the adsorbent temperature can cause significant departure from the isothermal uptake behavior when the heat of adsorption is moderately large. A criterion for validity of isothermal data analysis is given.

Keywords Adsorption · Kinetics · Non-isothermal · Forced convection · Heat removal

Introduction

Heat is evolved during the adsorption process. It is not easy to completely remove the heat from the adsorbent mass during the process. Consequently, non-isothermal analysis of the adsorption kinetic data is required for correct estimation of adsorptive mass transfer coefficients. Data analysis for non-isothermal integral adsorption tests, where the changes in the adsorbate loadings and the adsorbent temperatures are relatively large, require numerical solutions of coupled partial differential equations describing the mass and heat balances in the adsorbent particle (Brunovska et al., 1978, 1980). Such analysis can be complex and ambiguous. On the other hand, analytical solutions of non-isothermal models describing the mass and heat balance equations for various differential adsorption tests (DAT), where the changes in the adsorbate loadings and the adsorbent temperatures are deliberately kept small, have been obtained by many authors. Table 1 provides a list of several DAT models (Chihara et al., 1976; Ruthven et al., 1980; Sircar, 1983, 1994, 2006; Sircar and Kumar, 1984; Haul and Stremming, 1984; Sun et al., 1993; Silva et al., 2001; Brandani, 2003). The differential tests offer three key advantages:

- Linearization of the adsorption equilibrium with respect to changes in gas phase concentrations and adsorbent temperatures
- Decoupling of the effects of the above two variables on the kinetic process
- Simplification of data analysis by providing analytical solutions

The DAT models have demonstrated that (i) very small changes in the adsorbent temperature can cause a substantial departure of the adsorbate uptake curve from the corresponding isothermal uptake, if the isosteric heat of adsorption of the adsorbate gas is moderate to

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high, and (ii) analysis of non-isothermal uptake data by using an isothermal model severely underestimates the value of the mass transfer coefficient and can lead to incorrect information about the mechanism of sorption kinetics. Non-isothermal sorption process during the measurement of sorption kinetics should be taken as a rule unless (i) the kinetics is very slow or (ii) the process involves adsorption of a trace adsorbate from a carrier gas.

Removal of heat of adsorption by forced convection

One approach to remove the heat of adsorption from the adsorbent mass as soon as it is generated during the uptake process has been to flow the adsorbate gas (pure or mixture) over the adsorbent at a high rate. It is anticipated that heat loss from the adsorbent mass by forced convection would be sufficient to provide an isothermal sorption process. Consequently, an isothermal sorption kinetic model can be used for data analysis. This assumption has been used extensively by various authors using a "Differential Adsorption Bed (DAB)" for measurement of gas sorption kinetics (Carlson and Dranoff, 1987; Hu et al., 1994; King and Do, 1996; Qinglin et al., 2003). The validity of this assumption is investigated in this paper using a simple model of heat removal from an adsorbent mass undergoing a differential test in a flow system.

Mathematical model

It is assumed that the adsorbent chamber is a cylinder (Internal diameter = D, cm; Length = L, cm; Internal cross sectional area = $A = \pi D^2/4$, cm^2) which is packed with w gms of the adsorbent particles (radius = R_P, cm, bulk density = ρ_b, g/cc, void fraction = ε). The void volume (cc) of the packed adsorbent chamber is V_a. The chamber is immersed in a thermostated bath at temperature $T_\circ$. A gas mixture containing a single adsorbate (mole fraction = y°) and an inert carrier gas is passed over the adsorbent at pressure $P_\circ$ and temperature $T_\circ$ until the adsorbent is in equilibrium with the adsorbate. The specific equilibrium capacity (moles/g) of the adsorbate at $P_\circ$, $T_\circ$, and y° is n°. The molar gas flow rate based on the empty cross sectional area of the adsorbent chamber is Q (moles/cm^2/s). The adsorbate mole fraction of the gas is then differentially changed

Table 1 List of published models for non-isothermal differential adsorption tests

Author	Experimental method	Mass transfer resistance	Heat transfer resistance
Chihara, Suzuki, Kawazoe (1976)	Gravimetric sorption of a pure gas	Gas film outside sorbent particle	External film
Ruthven, Lee, Yucel (1980)	Same as above	Fickian micropore diffusion	Same as above
Sircar (1983)	Same as above	Linear driving force (LDF) model	Same as above
Sircar, Kumar (1984)	Same as above	Same as above	Both external film and thermal conductivity of the sorbent
Haul, Stremming (1984)	Same as above	Fickian diffusion	Same as above
Sun, Meunier, Karger (1993)	Frequency response technique (FRT) for a pure gas	Fickian micropore diffusion	External film
Sircar (1994)	Gravimetric sorption of a binary gas mixture	Linear driving force (LDF) model	Same as above
Silva, Da Silva, Rodrigues (2001); Brandani (2003)	Desorption of a single gas from a zero length column (ZLC)	Fickian micropore diffusion	Same as above
Sircar (2006)	Closed loop recycle method for sorption of a single adsorbate from carrier gas	Linear driving force model	Same as above

from y° to y^∞ and the process is continued until the adsorbent is equilibrated with the adsorbate at $P_\circ$, $T_\circ$, and y^∞ (specific equilibrium capacity $= n^\infty$). It is assumed that the gas flow rate is high (small residence time in the adsorption chamber) so that (i) the gas phase mole fraction of the adsorbate is constant ($= y^\infty$) inside the adsorber at all times, and (ii) the adsorbent temperature at any time t [$= T(t)$] is uniform through out the adsorbent mass during the uptake process.

A heat balance for the above- described differential uptake process yields:

$$\frac{d\theta(t)}{dt} = -\lambda\theta + \psi\frac{dn(t)}{dt} \tag{1}$$

$$\lambda = \left[\frac{AQC_g + ah}{wC_S}\right] = \left[\frac{QC_g}{LC_S\rho_b} + \frac{4h}{DC_S\rho_b}\right];$$
$$\psi = \left[\frac{q^o}{C_S}\right] \tag{2}$$

where $\theta\ (t)[= \{T(t) - T_\circ\}]$ is the change in the adsorbent temperature at time t during the uptake process, and $n(t)$ is the specific amount adsorbed at time t. The value of $\theta(t)$ is very small for a differential test. C_g and C_S are, respectively, the heat capacities of the gas (cal/mole/K) and the adsorbent (cal/g/K). The variables a ($= \pi DL$, cm^2) and h (cal/cm^2/s/K) are, respectively, the external heat transfer area of the adsorbent chamber and the effective heat transfer coefficient for heat loss from the adsorbent to the constant temperature b$ath.q^\circ$ (cal/mole) is the isosteric heat of adsorption of the adsorbate at loading n° and temperature $T_\circ$.

The parameter λ in Eq. (2) is the over-all characteristic time constant (s^{-1}) for heat removal from the adsorbent mass. It consists of two components: $\lambda_1 = [QC_g/LC_S(\rho_b)]$ and $\lambda_2 = [4h/DC_S(\rho_b)]$, representing the time constants for heat removal from the adsorbent mass by forced convection and that by heat loss through the walls of the adsorber, respectively.

It is further assumed that the Linear Driving Force (LDF) model describes the kinetics of adsorption for the adsorbate gas. The model is mathematically simple and most frequently used in adsorptive process design (Sircar and Hufton, 2000):

$$\frac{dn(t)}{dt} = k[n^*(t) - n(t)] \tag{3}$$

where, k(s^{-1}) is the LDF mass transfer coefficient for the adsorbate gas at a loading of n° and temperature $T_\circ$. $n^*(t)$ is the specific equilibrium amount adsorbed at $P_\circ$, $T(t)$, and y^∞.

For a differential test, $n^*(t)$ is given by (isotherm linearization and thermodynamics) (Sircar, 1983):

$$[n^*(t) - n^o] = aP_\circ[y^\infty - y^o] + b\theta;\ a = \left[\frac{\partial n^*}{\partial p}\right]_T;$$
$$b = \left[\frac{\partial n^*}{\partial T}\right]_p = -\left[\frac{aP_oy^0q^0}{RT_0^2}\right] \tag{4}$$

where $p(= P_\circ y)$ is the partial pressure of the adsorbate gas. The variables $a(> 0)$ and $b(< 0)$ are, respectively, the partial pressure and temperature coefficients of the adsorbate equilibrium isotherm evaluated at the initial equilibrium conditions (n°, $T_\circ$) of the test. R is the gas constant.

Equations (1)–(4) can be combined to obtain:

$$\frac{d^2\theta(t)}{dt^2} + [\lambda + k(1 - b\psi)]\frac{d\theta(t)}{dt} + k\lambda\theta(t) = 0 \tag{5}$$

Equation (5) can be integrated to obtain analytical expressions for fractional uptake, $f(t)$, of the adsorbate gas and the adsorbent temperature, $\theta(t)$, as functions of time (t) using the appropriate boundary conditions [$f(t \to 0) = 0$, $f(t \to \infty) = 1$, and $\theta\ (t \to 0, \infty) = 0$]:

$$f(t) = \frac{[n(t) - n^0]}{[n^\infty - n^0]} = \frac{B}{\lambda\sqrt{A^2 - 4B}}\left\{\left[\frac{\lambda + r_2}{r_2}\right]\left[1 - \exp(r_2t) - \left[\frac{\lambda + r_1}{r_1}\right][1 - \exp(r_1t)]\right\}\right. \tag{6}$$

$$\theta(t) = \frac{\psi\Delta(n^0)}{\lambda}\left\{\frac{B}{\sqrt{A^2 - 4B}}\right\}[\exp(r_1t) - \exp(r_2t)] \tag{7}$$

The key variables of Eqs. (6) and (7) are given by:

$$A = [\lambda + k(1 - b\psi)];\ B = k\lambda\quad;$$
$$r_1 = \frac{-A + \sqrt{A^2 - 4B}}{2};\ r_2 = \frac{-A - \sqrt{A^2 - 4B}}{2}$$

where r_1 and r_2 are the roots of the second order ordinary differential Eq. (5).

The maximum (or minimum) value of $\theta(t)$ profile is θ_m. It occurs at time $t = t_m$:

$$\theta_m = \frac{\psi\,\Delta(n^0)}{\lambda}\left\{\frac{B}{\sqrt{A^2-4B}}\right\}\left[r_1\left(\frac{r_2}{r_1}\right)^{z} - r_2\left(\frac{r_2}{r_1}\right)^{z-1}\right],$$
$$z = \frac{r_1}{r_1-r_2}; \quad t_m = \frac{\ln(r_2/r_1)}{r_1-r_2} \tag{8}$$

The variable Δ $[= (\frac{n^\infty - n^0}{n^0}) = \frac{aP_o(y^\infty - y^0)}{n^0}]$ in Eqs. (7) and (8) represents the net fractional change in the adsorbent loading of the adsorbate gas during the differential test.

It should be mentioned here that non-isothermal gas sorption kinetics by a differential closed-loop recycle method was studied in a recent publication (Sircar, 2006). Equation (5) above is a limiting case of Eq. (8) in that reference for $\beta \rightarrow 0$, which corresponds to the case where the volume of the closed-loop system approaches infinity.

Special case of isothermal system

For an isothermal adsorption process, where $\{n^*(t) - n^\circ\} = aP_\circ\{y^\infty - y^\circ\}$, Eq. (3) can be integrated to obtain:

$$f(t) = \frac{n(t) - n^0}{n^\infty - n^0} = 1 - \{\exp[-kt]\} \tag{9}$$

Equation (9) shows that a plot of ln $[1 - f(t)]$ against t will be a straight line with a slope equal to $[-k]$ for the isothermal case.

Approximate isothermal uptake behavior

It can be shown that Eq. (6) approximately reduces to Eq. (9) under the following condition:

$$-b\psi = +\frac{aP_o y^o (q^o)^2}{C_S R (T_o)^2} \ll 1 \tag{10}$$

The criterion (10) is generally satisfied when the adsorbate gas concentration is very low ($y^\circ \ll 1$, trace level, ppm). In other words, isothermal analysis of uptake data from a differential test may be justified only for sorption of adsorbate gases in trace concentrations. Otherwise, isothermal uptake behavior should not be taken for granted.

Case studies of heat removal from an adsorbent by forced convection

The effect of the heat of adsorption on non-isothermal uptake of an adsorbate in a differential flow system was examined by using Eqs. (6) and (7) for sorption of 5.0 mole % C_2H_6 from inert Helium on 5 A zeolite at 323 K ($T_\circ$) and a total gas pressure of 1.0 atm ($P_\circ$). The equilibrium adsorption isotherm for C_2H_6 on the zeolite can be described by the Langmuir model (Ruthven and Loughlin, 1972; Sircar and Kumar, 1983):

$$n^* = \frac{mcP_o y^o}{1 + cP_o y^o}; \; c = c^* \exp(q^o/RT_o);$$
$$a = \frac{mc}{[1 + cP_o y^o]^2} \tag{11}$$

where n^*(moles/g) is the equilibrium amount adsorbed at temperature $T_\circ(K)$, $P_\circ$ (atm) is the total gas pressure and y° is the gas phase mole fraction of the adsorbate. m (moles/g) is the saturation adsorption capacity for the adsorbate and q° (cal/mole) is the isosteric heat of adsorption. c (atm^{-1}) is the gas-solid interaction parameter, and c^* (atm^{-1}) is a constant. a (moles/gm/atm) is the gradient of the adsorption isotherm with respect to the adsorbate partial pressure ($p = P_\circ y_\circ$) at $T_\circ$.

The Langmuir model parameters for adsorption of C_2H_6 on 5A zeolite were given by:

$m = 1.4 \times 10^{-3}$ moles/g; $c^* = 5.97 \times 10^{-6}$ atm^{-1}; $q^\circ = 8800$ cal/mole (Ruthven and Loughlin, 1972; Sircar and Kumar, 1983). The properties of the helium at 1.0 atm and 323 K were: $C_g = 5.0$ cal/mole/K, viscosity $\mu_g = 5.19 \times 10^{-3}$ moles/cm/sec, thermal conductivity $\kappa_g = 3.77 \times 10^{-4}$ cal/sec/cm/K (Vargaftik, 1975).

It was assumed that the adsorbent chamber was cylindrical [$L = 3.0$ cm, $D = 1.0$ cm, $w = 1.65$ gms, $\varepsilon = 0.72$]. The adsorbent was initially equilibrated with 5.0% C_2H_6 (y°) in helium at $P_\circ$ and $T_\circ$. The gas phase C_2H_6 mole fraction was then changed by 5.0% $[= \{(y^\infty - y^\circ)/y^\circ\} \times 100]$ at the start of the DAT experiment. The heat loss through the walls of the adsorbent chamber was assumed to be controlled by the internal surface of the chamber. Thus, h could be

Table 2 Gas flow rates and characteristic time constants for heat removal

Specific gas flow rate (cm^3/g/s)	Q (mmoles/cm^2/s)	Re	λ_1 (s^{-1})	λ_2 (s^{-1})	λ (s$^{-1)}$
20.2	1.60	9.7	0.0173	0.00202	0.0193
60.6	4.80	28.7	0.0519	0.00248	0.0544
181.8	14.42	86.1	0.1560	0.00305	0.1591

calculated by the following correlation by Leva (1949):

$$[hD/\kappa_g] = 0.813[Re]^{0.19} \exp\{-12R_P/D\};$$
$$Re = 2R_P Q/\mu_g \qquad (12)$$

where Re is the particle Reynolds number for gas flow through the adsorbent chamber.

The key parameters of Eqs. (6) and (7) were estimated for this system as: $a = 4.66 \times 10^{-3}$ moles/g/atm, $\psi = 4.0 \times 10^4$ g·K/mole, $\Delta = 0.0279$, and $(-b\psi) = +0.395$. Thus criterion (10) was not satisfied and isothermal uptake for the system can not be granted. These parameters were used to generate the $f(t)$ and $\theta(t)$ profiles for different specific gas flow rates of 20.2, 60.6 and 181.8 (cc/gm. of adsorbent/s) in conjunction with a LDF mass transfer coefficient (k) of 0.20 sec^{-1}. Table 2 lists the values of Q, Re, and the characteristic time constants for heat removal at these flow rates.

It may be interesting to note from Table 2 that forced convection is the primary mechanism for heat removal from the adsorbent mass since $\lambda_1 \gg \lambda_2$ for all cases. This is because the external heat transfer coefficient (h) is relatively small and it is a weak function of Re, as given by Eq. (12). It should also be mentioned that heat loss by radiation is not important in the present case. However, radiation may contribute significantly to heat loss from an adsorbent mass in a gravimetric uptake experiment (Ruthven et al., 1980).

Figures 1 and 2 show the results of the model calculations. The sorption uptake curves are plotted as ln $[1 - f(t)]$ against t in Fig. 1. The corresponding $\theta(t)$ profiles are plotted in Fig. 2. The linear plot in Fig. 1 represents the isothermal uptake (Eq. (9)) for $k = 0.2$ s^{-1}. The non-linear uptakes of Fig. 1 (curves a–c) at different gas flow rates are caused by the non-isothermal kinetic process described by Fig. 2. Higher gas flow rate over the adsorbent facilitates heat removal form the adsorbent as

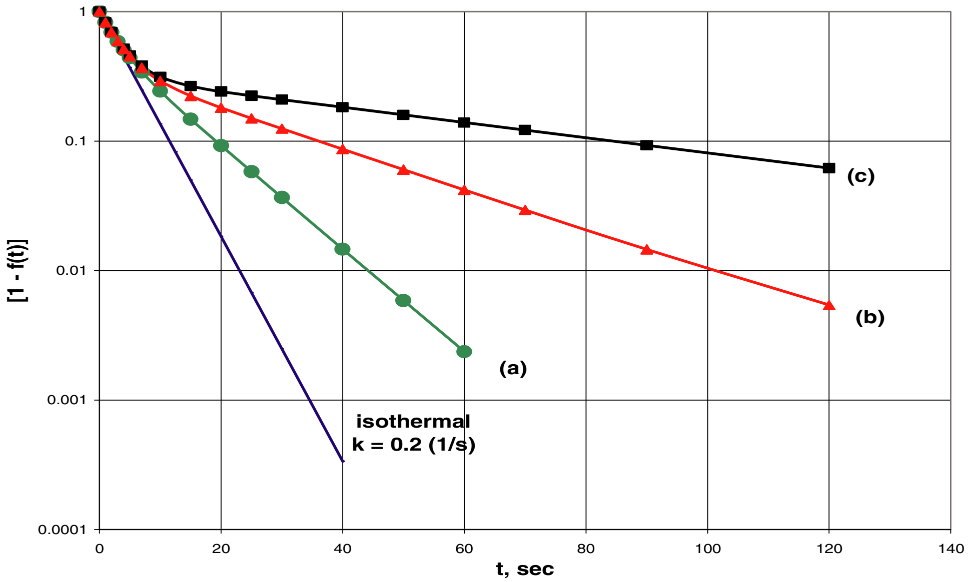

Fig. 1 Model uptake curves for a differential adsorption test with gas flow: (a) 181.8, (b) 60.6, (c) 20.2 cc/g/s

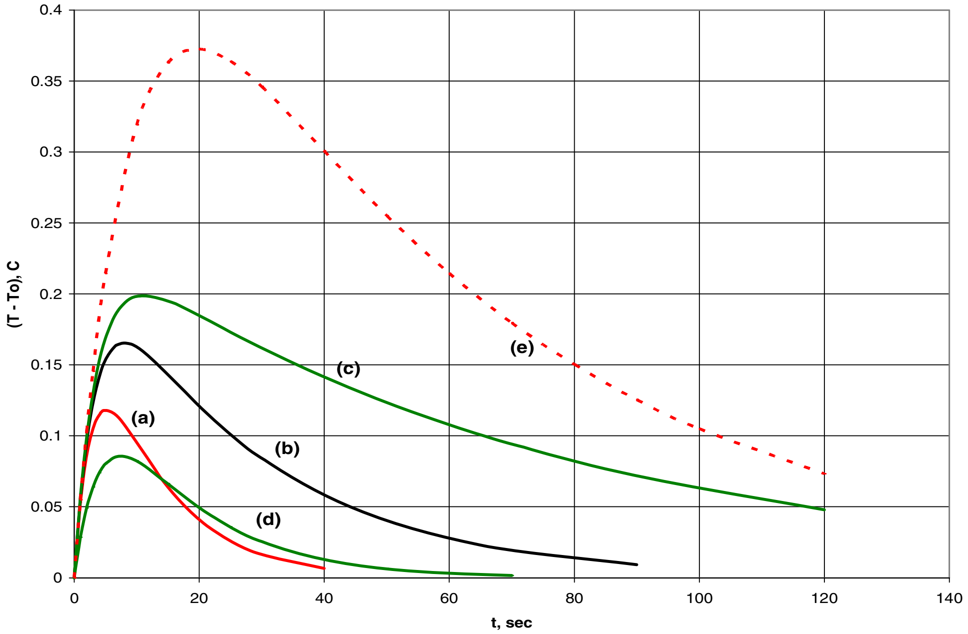

Fig. 2 Adsorbent temperature changes for the differential tests of Fig. 1

shown by Fig. (2), but isothermal operation may not be achieved.

Two most important observations from this exercise are that (i) the departure from the isothermal uptake behavior can be substantial even though the temperature changes in the adsorbent are very small ($<$0.2 C) when the heat of adsorption is moderate to high, and (ii) even a very high specific gas flow rate over the adsorbent ($>$100 cc/g/s) does not render isothermal behavior unless the adsorption kinetics is very slow.

Figure 3 compares the non-isothermal uptake curves for the above-described system for adsorbate mass transfer coefficients of $k = 0.2\ \mathrm{s}^{-1}$(closed triangles) and $k = 0.1\ \mathrm{s}^{-1}$ (closed squares). They were calculated using a high specific gas flow rate of 181.8 cc/g/s (Re = 86.1). In both cases, the uptakes are significantly slower than the corresponding isothermal uptakes, which are described by the solid straight lines in Fig. 3. Thus, isothermal behavior can not be assumed at that high flow rate even when$k = 0.1\ \mathrm{s}^{-1}$. The adsorbent temperature change during the uptake for this case is described by curve *d* of Fig. 2 which shows that the maximum value of $\theta(t)$ plot is less than 0.08 C.

An interesting observation is that the non-isothermal uptake for $k = 0.1\ \mathrm{s}^{-1}$ in Fig. 3 can be described fairly well by a straight line (dashed line through the squares) with a slope equal to – 0.075 s^{-1} ($= -k$). Thus, it could be mistakenly assumed that the uptake was isothermal for this case. However, that assumption would underestimate the mass transfer coefficient by ∼25%.

The closed circles in Fig. 3 show the model calculations for uptake of dilute C_3H_8 from N_2 at a pressure of 1.0 atm (101.3 KPa) and a temperature of 303.1 K by an activated carbon using a DAT with gas flow. The experimental conditions and the adsorptive properties of the system used in the calculation were identical to those reported by Hu, Do and Rao for measuring the kinetics of sorption of C_3H_8 employing a “DAB” test (Hu et al., 1994). The carbon bed ($\rho_b = 0.733$ g/cc, $C_S = 0.3$ cal/g/K, $R_P = 0.2$ cm) was small ($w = 0.4$ g) and the gas flow rate was 1000 cc/minute (= 41.7 cc/g/s). The carbon was initially equilibrated with dilute C_3H_8($y^\circ = 0.0273$, $P_\circ y^\circ = 2.761$ KPa) with a specific loading of 2.8 mmoles/g. The gas phase concentration was then changed by 5.0%. The C_3H_8 adsorption isotherm on the carbon could be described by the Langmuir model ($m = 5.03$ mmoles/g, c at 303.1 K = 0.454 KPa^{-1}, $q^\circ = 5.6$ Kcal/mole). The estimated diffusivity (D) of C_3H_8 from the DAB test was $\sim 9.0 \times 10^{-9} \mathrm{m}^2/\mathrm{s}$, which corresponded to k ($\sim 15\ D/R_P^2$) = 0.0337 s^{-1}. The uptake of C_3H_8 in the DAB test was assumed to be isothermal because of the fairly high specific gas flow rate over the adsorbent (Hu et al., 1994).

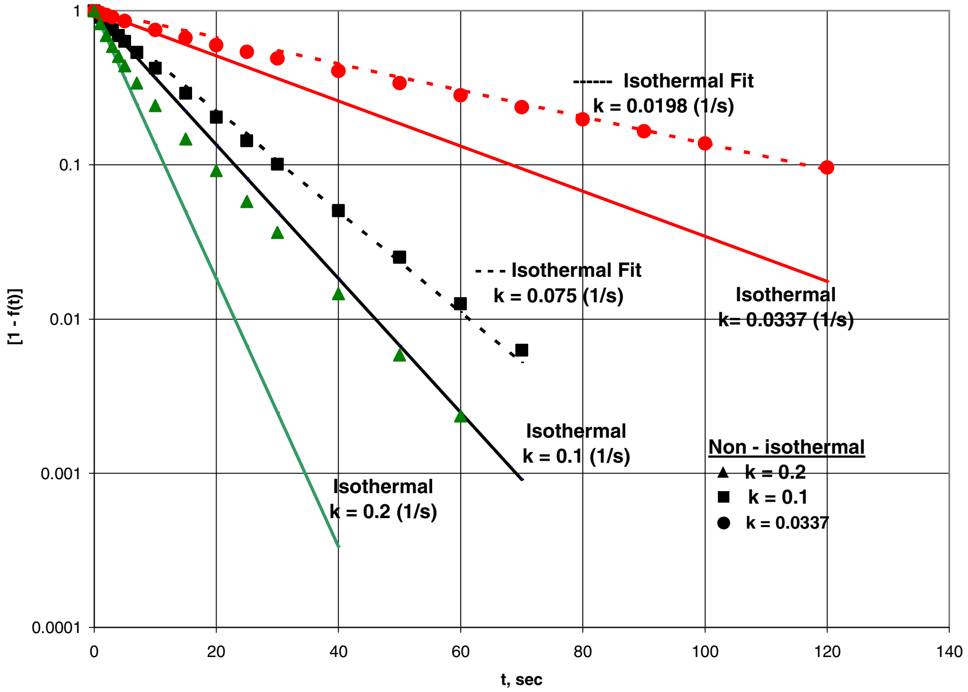

Fig. 3 Model uptake curves for DAT with gas flow: Effect of parameter *k*

The value of the parameter $(-b\psi)$ for the above-described system was calculated to be 1.0672. Hence, according to Eq. (10), isothermal uptake could not be assured. It was assumed that the carbon was placed in a thermostated tube ($L = D = 0.886$ cm). Thus, the value of the parameter λ was 0.0589 s^{-1}, and the Reynolds number for the system was 68.2. Eqs. (6) and (7) were then used to calculate the $f(t)$ and $\theta(t)$ functions for this case. The closed circles in Fig. (3) and the dashed curve (*e*) in Fig. (2) show the results.

It may be seen from Figs. (2) and (3) that (i) the uptake for this system was much slower than the corresponding isothermal uptake (solid line for $k = 0.0337\ \mathrm{s}^{-1}$), and (ii) the maximum adsorbent temperature change during the uptake process was $\sim$0.37 C (largest among the cases reported in Fig. 2). Clearly, the assumption of isothermal uptake for this system could not be valid even though the mass transfer coefficient for the adsorbate was low (smallest among the cases evaluated in this work). The isosteric heat of adsorption for this case was moderate, and the specific gas flow rate over the adsorbent was fairly large. The non-isothermal uptake for this case can also be described reasonably well by a straight line (shown by the dashed line through the closed circles in Fig. 3), which has a slope equal to – 0.0198 s^{-1}. In other words, the uptake can again be misjudged as an isothermal process. The assumption would, however, underestimate the actual mass transfer coefficient by $\sim$40% for this case.

The case studies presented in this work demonstrate that isothermal uptake by a differential adsorption test with gas flow over the adsorbent can not be taken for granted even when a fairly high specific gas flow rate is used. The departure from the isothermal uptake behavior can be significant when the adsorbate mass transfer coefficient is moderate to high, even though the adsorbent temperature changes are very small. The non-isothermal uptake data exhibited by a system with relatively slow kinetics can be approximately described by an isothermal uptake model. However, such erroneous data analysis can severely underestimate the adsorbate mass transfer coefficient.

It should be emphasized here that the kinetics of adsorption is a critical variable for design of adsorptive gas separation processes. For example, a 20% difference in the value of the mass transfer coefficient can introduce serious errors in the estimation of product recovery and productivity by a pressure swing adsorption process if the adsorption kinetics is relatively slow ($k < 0.2\ \mathrm{s}^{-1}$) (Hartzog and Sircar, 1995).

Summary

An analytical mathematical model is described to study the effectiveness of heat removal from an adsorbent mass by forced convection. It is shown that even a fairly high gas flow rate over the adsorbent may not be sufficient to produce isothermal uptake, particularly when the adsorbate mass transfer coefficient is moderately large. Non-isothermal uptakes can be approximately described by an isothermal model when the adsorption kinetics is relatively slow. However, such erroneous data analysis can severely underestimate the mass transfer coefficient. Isothermal uptake by a differential adsorption test should not be taken for granted unless the condition described by Eq. (10) is satisfied.

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