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Mass diffusion in a spherical microporous particle with thermal effect and gas-side mass transfer resistance

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Abstract

An analytical solution for mass diffusion in a spherical microporous particle experienced with a small step change of gaseous phase adsorbate concentration is obtained. The mass diffusion in the solid is assumed to be micropore diffusion controlled. Thermal effect and gas-side mass transfer resistance are considered. The governing equations are solved by using the Laplace transformation method. Three factors, α, β and γ are defined to govern the heat and mass transfer. α and β are relevant to the thermal effect and γ dominates the gas-side mass transfer resistance. The applicable ranges of three simplified models are discussed. A limiting solution with mass diffusivity approaching infinity is obtained. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Microporous solids are widely used in process of gas separation, such as adsorption of volatile organic compounds from air mixture by using activated carbon in industrial air pollution control, separation of nitrogen or oxygen from air by using molecular sieves in chemical gas plants or adsorption of water vapor from humid air by using silica gel in some drying or dehumidification processes etc. In general, the performance of a microporous solid (adsorbent) in adsorption of a gas (adsorbate) is determined by its equilibrium adsorption isotherms and dynamic sorption rate at various temperatures and concentrations. The former usually is obtained by performing experimental measurement in a gravimetric system. It is time-consuming, nevertheless there is almost no technical difficulty. The results of the measurement can be directly plotted on a diagram in which the adsorbed phase concentration of the adsorbate is represented as a function of gaseous phase concentration and temperature. Dissimilar to the former, the latter is a dynamic phenomenon which is strongly affected by the solid-side mass diffusivity of the adsorbent to the adsorbate. To predict the rate of an adsorption process accurately, the information of the mass diffusivity must be precisely provided. There are several ways to measure the mass diffusivity, generally speaking, they are much more complicated than that of the equilibrium adsorption isotherms. Conventional rate measurement does not directly yield the data of mass diffusivity. To obtain the value of mass diffusivity, an appropriate theoretical sorption model needs to be accompanied in the analysis. By assuming a value of mass diffusivity, a corresponding sorption uptake curve is acquired simply by evaluat-

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Nomenclature

a	external surface area per unit volume of adsorbent (m^{-1})
$B_{i,\,m}$	mass transfer Biot number, $h_m r_0/D$
c	gas concentration (kg m^{-3})
c_a	specific heat of adsorbent (kJ kg^{-1} K^{-1})
c_0	initial gas concentration (kg m^{-3})
c_∞	ambient gas concentration (kg m^{-3})
c^*	equilibrium gaseous phase concentration (kg m^{-3})
D	mass diffusivity (m^2 s^{-1})
h	convective heat transfer coefficient (W m^{-2} K^{-1})
h_m	convective mass transfer coefficient (m s^{-1})
ΔH	heat of sorption (kJ kg^{-1})
K	non-dimensional equilibrium constant, $\partial q^*/\partial c_s^*$
p	see Eq. (13)
q	adsorbate concentration in solid or $q^2 = -s$ (kg m^{-3})
q_m	average adsorbate concentration in solid (kg m^{-3})
q_n	characteristic roots
q_0	initial adsorbate concentration in solid (kg m^{-3})
q_∞	final adsorbate concentration in solid (kg m^{-3})
q^*	equilibrium adsorbed phase concentration (kg m^{-3})
Q	non-dimensional adsorbate concentration, $(q - q_0)/(q_\infty - q_0)$
Q_m	non-dimensional average adsorbate concentration, $(q_m - q_0)/(q_\infty - q_0)$
$\bar{Q}_m$	Q_m in Laplace domain
r	radial coordinate (m)
r_0	radius of particle (m)
s	Laplace coordinate
t	time (s)
T	temperature (K or °C)
T_0	ambient gas temperature (K or °C)

Greek symbols

α	time constant ratio, $har_0^2/(\rho_a c_a D)$
β	$\Delta H(\partial q^*/\partial T)/(\rho_a c_a)$
γ	$B_{i,\,m}/K$
γ'	$h_m \rho_a c_a/[(\partial q^*/\partial c^*)h]$
η	non-dimensional coordinate, r/r_0
θ	non-dimensional temperature, $-(\partial Q/\partial T) \times (T - T_0)$
$\bar{\theta}$	θ in Laplace domain
ρ	density (kg/m^3)
τ	non-dimensional time, tD/r_0^2
τ'	non-dimensional time, $hat/(\rho_a c_a)$

Subscripts

a	wet adsorbent
s	solid surface

ing the solution of the theoretical model. The theoretical result is then compared with the uptake curve which is obtained from experimental measurement. The value of the mass diffusivity adopted in the theoretical analysis, which provides the best match with the experimental result, is eventually taken as the true value of the mass diffusivity at a specific temperature and concentration. In case that the selected theoretical model is inappropriate in the first place, the matching will be mislead and the selected mass diffusivity turns out to be incorrect. The objective of this work is to develop a more precise theoretical model than those presently existing in predicting the process of an adsorption system. The solution of the model can be used either in determination of the mass diffusivity of an adsorbent to an adsorbate or in prediction of the uptake rate.

The related theoretical works in physical adsorption were summarized in details by Karger and Ruthven [1]. An adsorption system with thermal effect was analyzed by Lee and Ruthven [2]. The apparent mass diffusivity of a rapidly diffusing system obtained from the model would be much greater than that obtained from the simple isothermal model. The effect of intraparticle heat conduction on a sorption process was investigated by Haul et al. [3] and Sun et al. [4]. They found that, except for a few special cases, the lumped heat capacitance method is appropriate to be used in the energy balance. The uptake curve for a constant-pressure sorption system with two coupled intraparticle mass diffusion resistances was solved by Ruckenstein et al. [5]. A composite macroporous particle consisting of an assemblage of microporous particle such as zeolite, was considered to be the adsorbent. In the analysis, the system was assumed to be isothermal and the adsorption isotherms are linear.

The thermal effect of a constant-volume sorption process was investigated by Kocirik et al. [6]. In the work, the adsorbate concentration on the surface of the adsorbent was assumed to be in equilibrium with the ambient gaseous phase concentration and particle temperature. In an adsorption process, the thermal effect is due to the sorption heat dissipation. It influences both the solid-side diffusivity and the position of the sorption equilibrium. Thus, as compared to that of the isothermal sorption, the process is faster in the initial region and slower in the final region. The uptake curve of a constant-volume sorption system with two coupled intraparticle mass diffusion resistances was obtained by Ma et al. [7] and Lee [8]. Two limiting cases of the solution, individually corresponding to the macropore and micropore diffusion controlled systems, were obtained.

Some works for adsorption in packed bed were performed. The uptake curve of a non-isothermal sorption system under condition that the main resistance to mass transfer is from diffusion within the sample bed, rather than within the particle [9]. The mass diffusion model was established based on the particles on the top of the sample bed, it has been subjected to a small step change of the adsorbate pressure. Pesaran et al. [10] established a solid-side resistance model for analyzing the adsorption of water vapor from silica gel in a packed bed. The governing equations were solved numerically. San et al. [11,12] applied the solid-side resistance model in analyzing the adsorption performance of a packed bed in a periodic steady-state operation. The numerical result obtained from computer simulation was compared with the data obtained from experimental measurement for yielding a good agreement.

In this work, an analytical solution for a spherical adsorbent with both the thermal effect and external gas-side mass transfer resistance in an adsorption process is obtained. A uniform temperature distribution is assumed in the adsorbent and the lumped capacitance method is adopted in the energy balance. The adsorbate concentration in the solid is obtained by solving the governing equations with the Laplace transformation method. The solution is valid for a process initially with a small step change in the gaseous phase adsorbate concentration. The previous solution derived by Lee et al. [2] only considered the external gas-side heat transfer resistance, however the external gas-side mass transfer resistance was totally neglected. This is not suitable especially for the adsorption of an adsorbate from a mixture, such as the adsorption of water vapor from humid air or the adsorption of toluene from a toluene–air mixture. In such applications, the gas-side mass transfer resistance might play an important role in some circumstances. In the present analysis, a more delicate solution is derived and the effect of the external gas-side mass transfer resistance on the adsorption uptake curve is investigated.

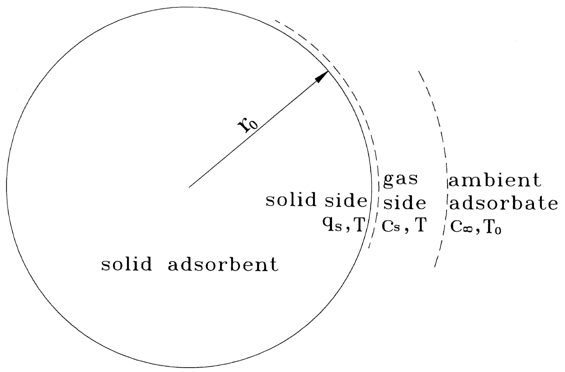

Fig. 1. A spherical microporous adsorbent.

2. Mathematical model

A homogeneous spherical microporous solid in adsorption of a gaseous adsorbate is considered (Fig. 1). The adsorbate concentration in the solid is initially assumed to be uniform and in equilibrium with the gaseous phase adsorbate. Suddenly a step change of the gaseous phase adsorbate is imposed on the system. The mass balance of the adsorbate in the solid can be expressed as follows [1]:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial q}{\partial r}\right)=\frac{\partial q}{\partial t} \tag{1}$$

with the initial and the boundary conditions,

(i) at $t=0$, $q=q_0$
(ii) at $r=0$, $\partial q/\partial r=0$
(iii) at $r=r_0$, $h_{\mathrm{m}}(c_\infty-c_{\mathrm{s}})=D(\partial q/\partial r)$

The average concentration of adsorbate in the solid is,

$$q_m=\frac{3}{r_0^3}\int_0^{r_0} qr^2\,\mathrm{d}r \tag{2}$$

The energy equation for the solid can be represented in the following form:

$$(-\Delta H)\frac{\mathrm{d}q_m}{\mathrm{d}t}=\rho_{\mathrm{a}}c_{\mathrm{a}}\frac{\mathrm{d}T}{\mathrm{d}t}+ha(T-T_0) \tag{3}$$

with the two initial conditions,

(i) at $t=0$, $T=T_0$
(ii) at $t=0$, $q_m=q_0$

In this work, the lumped-heat-capacitance method is adopted in the energy balance. This method is only valid for adsorption with a small heat transfer Biot number and generally this is the situation for most of the cases [10]. In Eq. (3), $(-\Delta H)$ is the heat of sorption which is a positive value in an adsorption process.

Eqs. (1)–(3) are a set of coupled non-linear partial differential equations with three unknowns, q, q_m, and

T. The non-linearity of the equations are due to the dependency of D on q and T, and the dependency of c_s on q_s and T. The mass diffusivity, D, is a physical property which governs the solid-side mass diffusion resistance. The concentration of gaseous phase adsorbate near the solid surface, c_s, is assumed to be in equilibrium with the adsorbed phase adsorbate on the solid surface. The two non-linearity effects can be neglected if the initial step change of the gaseous phase adsorbate concentration is small. If so, the mass diffusion coefficient, D, can be treated as a constant and the Taylor's expansion can be applied to $(c_\infty - c_s)$ in boundary condition (iii) of Eq. (1). Defining several non-dimensional groups, the above governing equations can be expressed in a linear form as follows:

$$\frac{1}{\eta^2}\frac{\partial}{\partial \eta}\left(\eta^2\frac{\partial Q}{\partial \eta}\right) = \frac{\partial Q}{\partial \tau} \tag{4}$$

with the initial and boundary conditions,

(i) at $\tau = 0$, $Q = 0$
(ii) at $\eta = 0$, $\partial Q/\partial \eta = 0$
(iii) at $\eta = 1$, $\frac{1}{\gamma}\frac{\partial Q}{\partial \eta} = (1 - Q) - \theta$

where

$$\gamma \equiv \frac{B_{i,\,m}}{K}, \quad K = \frac{\partial q^*}{\partial c_s^*}$$

The non-dimensional average concentration of adsorbate in the solid is,

$$Q_m = 3\int_0^1 Q\eta^2\,\mathrm{d}\eta \tag{5}$$

The non-dimensional energy equation is,

$$\beta\frac{\mathrm{d}Q_m}{\mathrm{d}\tau} = \frac{\mathrm{d}\theta}{\mathrm{d}\tau} + \alpha\theta \tag{6}$$

where

$$\alpha \equiv \frac{har_0^2}{\rho_a c_a D}, \quad \beta \equiv \frac{\Delta H}{\rho_a c_a}\left(\frac{\partial q^*}{\partial T}\right)$$

with the initial conditions,

$$\text{at } \tau = 0, \quad \theta = Q_m = 0$$

In Eq. (4), the chain rule, $(\partial q^*/\partial T) = -(\partial c_s^*/\partial T)/(\partial c_s^*/\partial q^*)$, has been used to yield the relationship in boundary condition (iii). For a small step change of the initial gaseous phase adsorbate, $(\partial q^*/\partial T)$ and $(\partial q^*/\partial c_s^*)$ can be assumed to be constants. Similarly, ρ_a and c_a also can be treated as constants. The two derivatives are individually used in defining β and γ. β and γ are two important factors to govern the characteristics of the adsorption process. The former indicates the magnitude of the thermal effect and the latter represents the importance of the gas-side mass transfer resistance. For an adsorption process with a low value of $(\partial q^*/\partial T)$, the value of β is also small and the adsorption uptake is no longer affected by the temperature variation. The mass balance equation and energy equation thus can be treated as two independent equations. Under the circumstance, the thermal effect can be neglected and the isothermal model is appropriate to be applied in predicting the uptake curve. For an adsorption process with a high value of γ, the gas-side mass transfer resistance will be small and the concentration boundary layer between the solid and fluid can be neglected. A high value of γ might be resulted from either a low value of K or a high value of $B_{i,\,m}$. The former represents the adsorption capability of the adsorbent and the latter indicates the relative magnitude between the gas-side mass transfer and solid-side mass diffusion. An adsorbent with a low value of K implies that on the surface of the particle an increase of the gas-side adsorbate concentration is nearly without having any influence on the solid-side adsorbate concentration. After a step change of the gas-side adsorbate concentration in the beginning of the process, the solid-side adsorbate concentration on the surface of the particle will remain almost unchanged. Thus, the gas-side mass transfer resistance is relatively small and the left-hand side of boundary condition (iii) in Eq. (4) can be neglected. If so, the factors affecting the adsorption uptake are mainly due to the solid-side mass diffusion resistance and the thermal effect. Based on the above explanation, it is appropriate to name the parameter, γ, as the overall mass transfer Biot number in the adsorption process.

In Eq. (6), α and β are two important factors governing the thermal effect. α can be rearranged into the form, $[(r_0^2/D)/(\rho_a c_a/ha)]$, which indicates the relative magnitude between the mass diffusion time constant and the heat transfer time constant. A high value of α may be due to either a large mass diffusion time constant or a small mass diffusion time constant. The case with a large mass diffusion time constant means the adsorption process is slow. If so, the released heat of sorption has sufficient time to be transferred away from the solid surface and the heat will not be accumulated in the solid to affect the uptake curve. Similarly, in the case with a small heat transfer time constant the surface heat convection will be strong and thus the thermal effect is relatively weak. In Eq. (6), β is defined as $[(\Delta H/\rho_a c_a)(\partial q^*/\partial T)]$ in which both ΔH and $\partial q^*/\partial T$ are negative values. According to the definition, β can be viewed as, due to the thermal effect, the decrease of the mass of the adsorbate on the surface of the particle for the adsorption of a unit mass of the adsorbate. Thus, a high value of β implies that the thermal effect is important.

2.1. Laplace transformation

The set of Eqs. (4)–(6) can be solved by using the Laplace transformation method. The solution of Eq. (4) in the Laplace domain is,

$$\bar{Q} = \frac{\sin(\sqrt{s}\eta)}{\eta}\,\frac{1/s - \bar{\theta}}{(1 - 1/\gamma)\sinh\sqrt{s} + 1/\gamma\sqrt{s}\cosh\sqrt{s}} \tag{7}$$

The average concentration of the adsorbate in the Laplace domain is,

$$\begin{aligned}\bar{Q}_m &= 3\int_0^1 \bar{Q}\eta^2\,\mathrm{d}\eta \\ &= \frac{3/s\left(\sqrt{s}\cosh\sqrt{s} - \sinh\sqrt{s}\right)\left(1/s - \bar{\theta}\right)}{(1 - 1/\gamma)\sinh\sqrt{s} + 1/\gamma\sqrt{s}\cosh\sqrt{s}}\end{aligned} \tag{8}$$

Eqs. (7) and (8) still contain $\bar{\theta}$ which can be obtained by solving the energy equation. The energy equation in the Laplace domain is,

$$\beta\left[s\bar{Q}_m - Q_m(0)\right] = \left[s\bar{\theta} - \theta(0)\right] + \alpha\bar{\theta} \tag{9}$$

From the initial conditions, both $Q_m(0)$ and $\theta(0)$ are zero. Thus, Eq. (9) can be expressed as follows:

$$\bar{\theta} = \left(\frac{\beta s}{s + \alpha}\right)\bar{Q}_m \tag{10}$$

Eqs. (8) and (10) can be solved simultaneously and it yields $\bar{Q}_m$, $\bar{\theta}$ and $\bar{Q}$ as follows:

$$\bar{Q}_m = \frac{3(s + \alpha)(p\cosh p - \sinh p)}{s^2\left\{(s + \alpha)\left[(1 - 1/\gamma)\sinh p + 1/\gamma(p\cosh p)\right] + 3\beta(p\cosh p - \sinh p)\right\}} \tag{11}$$

$$\bar{\theta} = \frac{3\beta(p\cosh p - \sinh p)}{s\left\{(s + \alpha)\left[(1 - 1/\gamma)\sinh p + 1/\gamma(p\cosh p)\right] + 3\beta(p\cosh p - \sinh p)\right\}} \tag{12}$$

$$\bar{Q} = \frac{\sin(\eta q)}{\eta\sin q}\,\frac{(s + \alpha)}{s\left\{(s + \alpha)\left[(1 - 1/\gamma)\sinh p + 1/\gamma(p\cosh p)\right] + 3\beta(p\cosh p - \sinh p)\right\}} \tag{13}$$

where

$$s = p^2 = -q^2$$

Eqs. (11)–(13) have infinite series poles which are determined by the roots of the following equation,

$$\frac{1}{q_n\cot q_n - 1} = -\frac{1}{\gamma} + \frac{3\beta}{q_n^2 - \alpha} \tag{14}$$

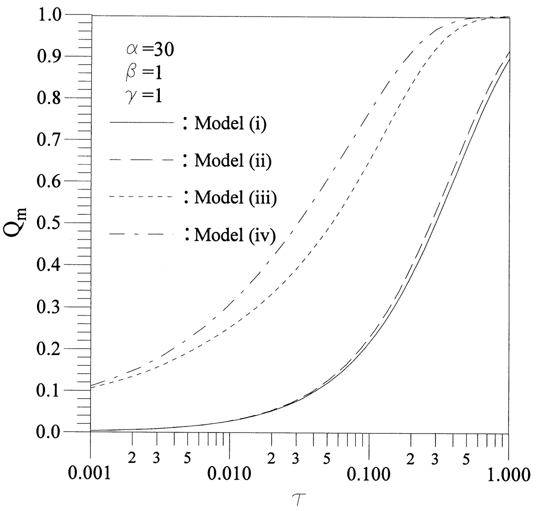

Fig. 2. Comparison of uptake curves for four analytical solutions ($\alpha = 30$, $\beta = 1$, $\gamma = 1$).

Eq. (14) is the characteristic equation of the governing equations. The roots, q_n, can be solved by using the Newton–Raphson's scheme for a set of α, β and γ. In Eq. (14), q_n ($n = 1, 2, \ldots, \infty$) are positive values. The magnitude of the first root, q_1, usually strongly affects the sorption rate in an adsorption process. All the three equations (Eqs. (11)–(13)) appear to have a simple pole at $s = 0$. However, checking by using the L'Hospital's rule, the simple pole at $s = 0$ in Eq. (12) can be removed.

The inverse Laplace transformation of Eqs. (11)–(13), after rearrangement, is individually represented as follows:

$$Q_m(\tau) = 1 - \sum_{n=1}^{\infty} \frac{\dfrac{3}{q_n^4}\exp\left(-q_n^2\tau\right)}{\dfrac{3\beta}{\left(q_n^2-\alpha\right)^2} + \dfrac{1}{2}\left[\left(-\dfrac{1}{\gamma} + \dfrac{3\beta}{q_n^2-\alpha}\right)^2 + \dfrac{1}{q_n^2}\left(1 - \dfrac{1}{\gamma} + \dfrac{3\beta}{q_n^2-\alpha}\right)\right]}$$

$$\theta(\tau) = \sum_{n=1}^{\infty} \frac{-\dfrac{3\beta}{q_n^2\left(q_n^2-\alpha\right)}\exp\left(-q_n^2\tau\right)}{\dfrac{3\beta}{\left(q_n^2-\alpha\right)^2} + \dfrac{1}{2}\left[\left(-\dfrac{1}{\gamma} + \dfrac{3\beta}{q_n^2-\alpha}\right)^2 + \dfrac{1}{q_n^2}\left(1 - \dfrac{1}{\gamma} + \dfrac{3\beta}{q_n^2-\alpha}\right)\right]} \tag{16}$$

$$Q(\eta, \tau) = 1 + \sum_{n=1}^{\infty} \frac{\dfrac{\sin(\eta q_n)}{\eta q_n^2 \sin q_n}\left(-\dfrac{1}{\gamma} + \dfrac{3\beta}{q_n^2-\alpha}\right)\exp\left(-q_n^2\tau\right)}{\dfrac{3\beta}{\left(q_n^2-\alpha\right)^2} + \dfrac{1}{2}\left[\left(-\dfrac{1}{\gamma} + \dfrac{3\beta}{q_n^2-\alpha}\right)^2 + \dfrac{1}{q_n^2}\left(1 - \dfrac{1}{\gamma} + \dfrac{3\beta}{q_n^2-\alpha}\right)\right]} \tag{17}$$

Many previously derived solutions [1] are the special cases of the problem in the present consideration. Three special cases are individually considered in the following:

(i) Isothermal adsorption without external film mass transfer resistance (simple isothermal model):

$$Q_m(\tau) = 1 - 6\sum_{n=1}^{\infty}\frac{\exp\left(-q_n^2\tau\right)}{q_n^2} \quad \text{for} \quad \alpha/\beta \rightarrow \infty, \gamma \rightarrow \infty \tag{18}$$

The characteristic equation is,

$$q_n = n\pi \tag{19}$$

(ii) Isothermal adsorption with external film mass transfer resistance:

$$Q_m(\tau) = 1 - \sum_{n=1}^{\infty}\frac{6\gamma^2\exp\left(-q_n^2\tau\right)}{q_n^2\left[q_n^2 + \gamma(\gamma-1)\right]} \quad \text{for } \alpha \rightarrow \infty \text{ or } \beta = 0 \tag{20}$$

The characteristic equation is,

$$q_n \cot q_n + \gamma - 1 = 0 \tag{21}$$

(iii) Adsorption with thermal effect, but without external film mass transfer resistance:

$$Q_m(\tau) = 1 - \sum_{n=1}^{\infty} \frac{\dfrac{3}{q_n^4}\exp\left(-q_n^2\tau\right)}{\dfrac{3\beta}{\left(q_n^2-\alpha\right)^2} + \dfrac{1}{2}\left[\left(\dfrac{3\beta}{q_n^2-\alpha}\right)^2 + \dfrac{1}{q_n^2}\left(1 + \dfrac{3\beta}{q_n^2-\alpha}\right)\right]}$$

for $\gamma \rightarrow \infty$

The characteristic equation is,

$$\frac{1}{q_n \cot q_n - 1} = \frac{3\beta}{q_n^2 - \alpha} \tag{23}$$

In Eq. (22), the characteristic equation has been used to rearrange the original solution into the present form. In fact, it is the same as that derived by Lee et al. [2].

2.2. Film resistance controlled adsorption ($D \rightarrow \infty$)

For the case with the value of D approaching infinity, the external film heat and mass transfer resistances will dominate the sorption rate. For this limiting case, the two governing equations can be expressed as follows:

$$\frac{\mathrm{d}Q_m}{\mathrm{d}\tau'} = \gamma'(1 - Q_m) - \gamma'\theta \tag{24}$$

$$\beta\frac{\mathrm{d}Q_m}{\mathrm{d}\tau'} = \frac{\mathrm{d}\theta}{\mathrm{d}\tau'} + \theta \tag{25}$$

where

$$\tau' = \tau\alpha, \quad \gamma' = 3\gamma/\alpha$$

The two initial conditions are,

$$\text{at } \tau' = 0, \quad \theta = Q_m = 0$$

Eq. (24) is the mass balance equation which is similar to the third boundary condition of Eq. (4). Eq. (25) is the energy equation which is similar to Eq. (6). Eqs. (24) and (25) are solved simultaneously by using the Laplace transformation method. The result is shown as follows:

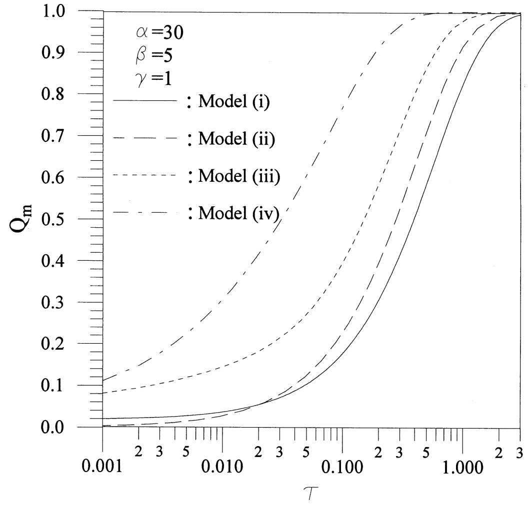

Fig. 3. Uptake curves ($\alpha = 30$, $\beta = 5$, $\gamma = 1$).

$$Q_m(\tau') = 1 + \sum_{i=1}^{2} \frac{\gamma'(s_i + 1)\exp(s_i\tau')}{(s_i)^2 - \gamma'} \tag{26}$$

where the two roots are,

$$s_{1,2} = \frac{-(1 + \gamma' + \gamma'\beta) \pm \sqrt{(1 + \gamma' + \gamma'\beta)^2 - 4\gamma'}}{2} \tag{27}$$

The above solution also can be obtained directly from Eqs. (14) and (15) simply by letting $D \to \infty$.

3. Results

The characteristics of the adsorption uptake curve and non-dimensional temperature variation, as shown in Eqs. (15)–(17), are affected by the three factors, α, β and γ. In this work, the solution of the adsorption uptake curve is evaluated for various α, β and γ. Fig. 2 shows the adsorption uptake curves ($\alpha = 30$, $\beta = \gamma = 1$) calculated by using four different models. In the diagram, Model (i) is the non-isothermal model with external film mass transfer resistance; Model (ii) is the isothermal model with external film mass transfer resistance; Model (iii) is the non-isothermal model without external film mass transfer resistance and Model (iv) is the simple isothermal model without external film mass transfer resistance. As indicated in Fig. 2, the uptake curve obtained from Model (ii) is very close to that obtained from Model (i). This implies that for this specific operating condition the thermal effect only slightly affects the uptake curve. Thus, the thermal effect can be neglected and Model (i) can be replaced by Model (ii) in the analysis. As far as the results obtained from Model (iii) and Model (iv), a significant discrepancy is observed as they are compared with the result obtained from Model (i). Hence, it verifies that the external mass transfer resistance plays an important role in this case.

Fig. 3 shows the adsorption uptake curves for the case with $\alpha = 30$, $\beta = 5$ and $\gamma = 1$. The operating condition in Fig. 3 is similar to that in Fig. 2, except that the value of β in Fig. 3 is greater than that in Fig. 2. The case with a higher value of β implies that the temperature variation of the adsorbent is higher during the adsorption. Thus, the influence of the thermal effect on the uptake curve is also more significant. Fig. 3 clearly shows the deviation between the result obtained from Model (i) and that obtained from Model (ii). The results obtained from Model (iii) and Model (iv), similar to that in Fig. 2, still reveal a large discrepancy to that obtained from Model (i). Both Figs. 2 and 3 indicate that the external film mass transfer resistance is important and thus it can not be neglected in the analysis.

Fig. 4 shows the effect of γ on the adsorption uptake curve. The value of α and β in Fig. 4 is the same as those in Fig. 2. However, the value of γ in Fig. 4 is two times of that in Fig. 2. Similar to the result in Fig. 2, the uptake curve obtained from Model (ii) is close to that obtained from Model (i). However, the discrepancy between the two corresponding uptake curves in Fig. 4 is slightly greater than that in Fig. 2. An adsorption system with a larger value of γ means that the external film mass transfer coefficient is also larger. Thus, the external film mass transfer resistance is smaller and the adsorption rate is faster. It turns out that more heat is generated in a certain time period. Hence, the thermal effect for the case with a larger value of γ is more significant than that with a smaller value. This explains why the discrepancy of the two curves in Fig. 4 is greater than that in Fig. 2. In Fig. 4, since the value of γ is small, the external film mass transfer resistance cannot be neglected. Accordingly, both Model (iii) and Model (iv) are still not applicable in this case. Also, owing to a higher value of γ, the adsorption uptake curve obtained from Model (i) in Fig. 4 reaches the equilibrium condition much faster than that in Fig. 2.

Fig. 5 illustrates the effect of γ on the adsorption uptake curve for $\alpha = 30$ and $\beta = 5$. The condition in Fig. 5 is same as that in Fig. 3, except that the value of γ has been largely increased 40 times. Since the increase in the value of γ is rather large, the external film mass transfer resistance becomes no longer important. Under this circumstance, the result obtained from Model (iii) is very close to that obtained from Model (i). However, in Fig. 5 the value of α remains relatively small and the value of β is still large. The thermal effect cannot be neglected in this case. Thus, the results obtained from Model (ii) and

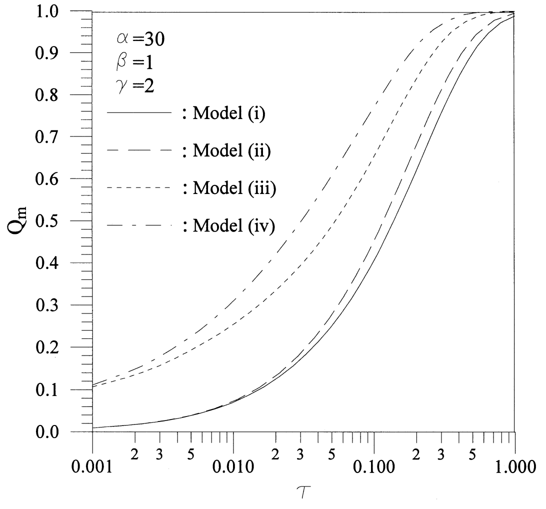

Fig. 4. Uptake curves ($\alpha = 30$, $\beta = 1$, $\gamma = 2$).

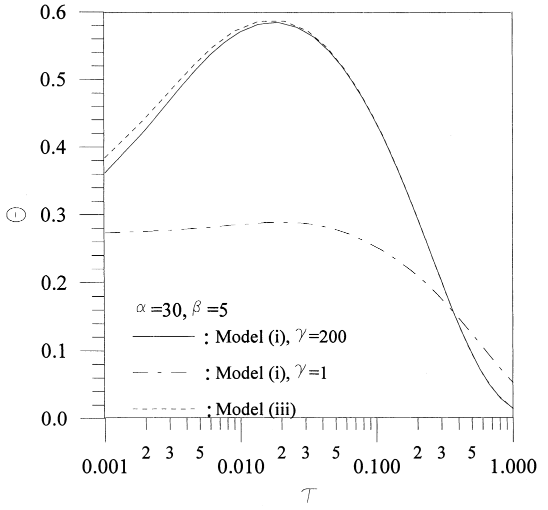

Fig. 6. Effect of γ on non-dimensional temperature variation.

Model (iv) apparently do not match with that obtained from Model (i). Due to a smaller value of the external film mass transfer resistance, the sorption rate obtained from Model (i) in Fig. 5 is faster than that in Fig. 3.

Fig. 6 represents the non-dimensional temperature variation for the two cases individually considered in Figs. 3 and 5. The result reveals that the solid temperature, for the case with a larger value of γ, is also higher. Fig. 6 also shows the temperature variation evaluated by using Model (iii). Again, it appears that Model (iii) is only applicable to the case with a high value of γ.

Fig. 7 represents the uptake curves for the case with $\alpha = 30$, $\beta = 0.5$ and $\gamma = 100$. As compared with the condition in Fig. 4, the value of β in Fig. 7 is reduced to a half and the value of γ is increased to 100. As mentioned earlier, the importance of the thermal effect decreases with the value of β. For the case considered in Fig. 7, the thermal effect becomes minor and the external film mass transfer resistance is small. It turns out that both the thermal effect and external film mass transfer resistance can be neglected. Hence, the simple isothermal model (Model (iv)) is valid. In Fig. 7, the deviation among the four uptake curves, individually calculated by using the four models, appears to be small.

Many calculations, similar to those in Figs. 2–7, are performed for various values of α, β and γ. The results

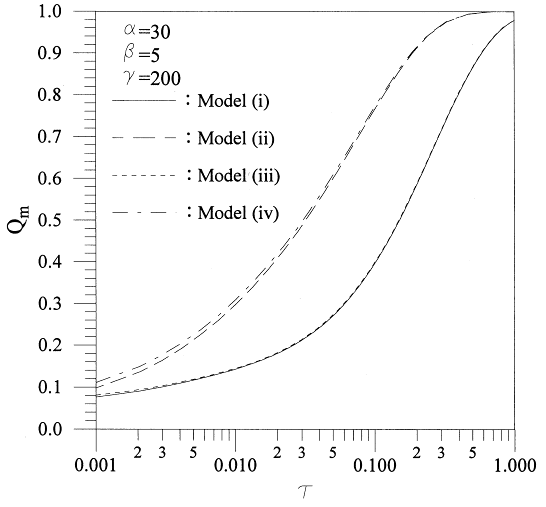

Fig. 5. Uptake curves ($\alpha = 30$, $\beta = 5$, $\gamma = 200$).

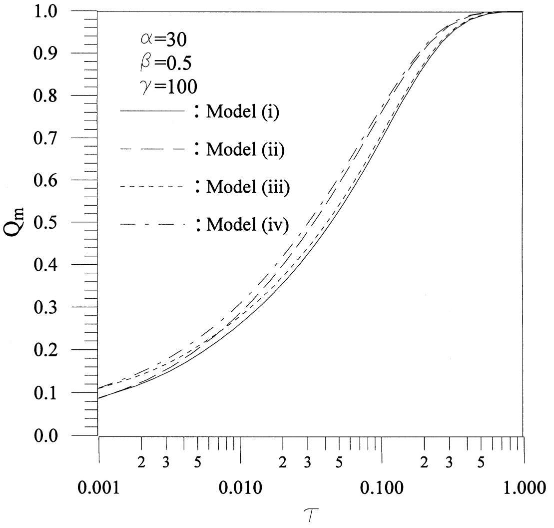

Fig. 7. Uptake curves ($\alpha = 30$, $\beta = 0.5$, $\gamma = 100$).

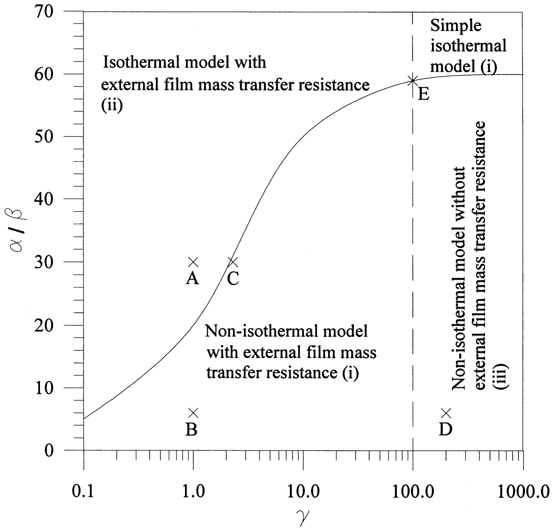

Fig. 8. Operating range for various adsorption models.

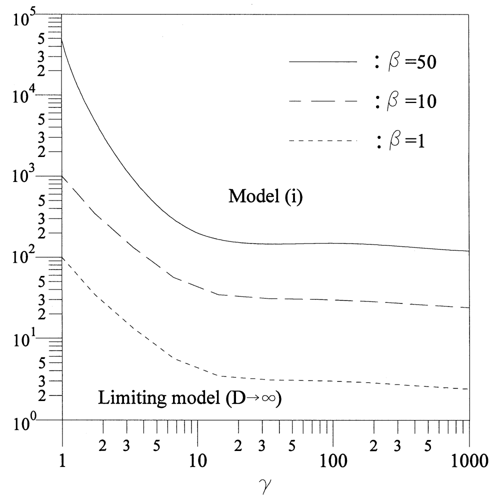

Fig. 9. Operating range for the limiting solution with $D \rightarrow \infty$.

are analyzed and summarized in Fig. 8. As shown in the diagram, the applicable range of the four models is indicated individually. The five points, A, B, C, D and E in the diagram individually corresponds to the case considered in Figs. 2–7. The division of the regions in Fig. 8 is based on the criterion that the maximum deviation of the non-dimensional average adsorbate concentration, Q_m, on the uptake curves obtained from various models is greater than 10%. The non-isothermal model with external film mass transfer resistance (Model (i)) is valid to the entire region in Fig. 8. For the case with the value of α/β above that on the curve, the isothermal model with external film mass transfer resistance (Model (ii)) is suitable. The value of α indicates the magnitude of the convective heat transfer during the adsorption process. The higher the value of α, the stronger the heat convection and the weaker the thermal effect. The value of β indicates the magnitude of the released heat for an adsorption system. The lower the value of β, the lesser the released heat and similarly the weaker the thermal effect. Consequently, for an adsorption process with a large value of α/β, the thermal effect is minor. This phenomenon also had been pointed out by Lee and Ruthven [2]. As shown in Fig. 8, as the value of α/β exceeding 60 and the value of γ approaching infinity, the thermal effect can be neglected and the simple isothermal model is appropriate to be used in predicting the adsorption uptake curve. This conclusion is also the same as that reported by Lee and Ruthven [2]. Besides the ratio of α/β, the thermal effect is also influenced by the magnitude of γ. As defined in the beginning, γ is proportional to the external film mass transfer coefficient, h_m. An adsorption process with a larger value of h_m implies that the sorption rate on the surface of the solid is faster. Thus, the heat generation rate is larger and the thermal effect is more significant. This explains why the point on the curve in Fig. 8 has a higher value of α/β for a larger value of γ. As shown in the diagram, for the case with the value of γ less than 0.l, the thermal effect is minor as long as the value of α/β is greater than 6. In Fig. 8 it also shows that the simple isothermal model (Model (iv)) is only valid for a small operating region on the upper right corner. In this region, γ is greater than 100 and the ratio of α/β is grater than 60.

In real applications, the corresponding values of α/β and γ of an adsorption system will fit into one of the four regions in Fig. 8. One example, regarding the adsorption of toluene in a granular activated carbon is illustrated. The activated carbon particle is in equilibrium with a toluene–air mixture. The equivalent diameter of the particle is 2.42 mm. The initial toluene concentration is 5 ppm and suddenly the toluene concentration is changed to 10 ppm. It assumes that the air is not involved in the adsorption process and the temperature of the mixture maintains at 27°C. The constant pressure specific heat and density of the activated carbon particle are respectively 1.05 kJ/kg-K and 898 kg/m^3. The heat of sorption is 600 kJ/kg [12]. $(\partial q^*/\partial T)$ is -3.15 kg/m^3-K and the value of K is 2.272 $\times$ 10^6. The solid-side mass diffusivity is 8.45 $\times$ 10^{-11} m^2/s and the molecular diffusivity of toluene in the air is 8.14 $\times$ 10^{-6} m^2/s. The Nusselt number is 2.0 which is the value corresponding to the case for a hot sphere in a cold still fluid. The analogy between heat transfer and mass transfer is adopted. The value of α is calculated to be 986; the value of β is 2 and γ is 0.042. In Fig. 8, the set of the values of α/β and γ is in the region of Model (ii). Thus the external mass transfer resistance is important and the thermal effect can be neglected.

Fig. 9 illustrates the operating region of the model without the internal mass diffusion resistance ($D \rightarrow \infty$). Similarly, many calculations have been performed for various values of α, β, and γ in order to summarize the results in the diagram. As shown in Fig. 9, there are three curves which indicate the boundary of the operating region for this limiting case with β of 1, 10 and 50, respectively. The area above every individual curve indicates the operating region for the non-isothermal model with the external film mass transfer resistance (Model (i)). The area below the individual curve represents the operating region of the limiting solution. The division of the two regions is based on the same criterion as that in Fig. 8. In Fig. 9, in the region for the value of γ less than 10, all the three curves descend rapidly. This implies that, for a fixed value of α and β, the lower the value of γ, the closer the process to the case without the internal mass diffusion resistance. From the definition, the convective mass transfer coefficient, h_m, increases with γ. For an adsorption process with a relatively low value of the convective mass transfer coefficient (γ is small), the external film mass transfer resistance will be large and the internal mass diffusion resistance will be relatively less important than the external film mass transfer resistance. Consequently, the external film mass transfer will dominate the shape of the uptake curve. It turns out that the result obtained by analyzing the limiting model ($D \rightarrow \infty$) will be close to that obtained by analyzing Model (i). Fig. 9 also reveals that for a fixed value of α and γ, the higher the value of β, the closer the process to the limiting case. For the case with a relatively high value of β, the thermal effect will be more important than the internal mass diffusion resistance. Furthermore, if both the values of α and γ are small enough, the internal mass diffusion resistance can be neglected. In such case, the limiting model will also be appropriate to be used in the analysis. For the adsorption of toluene in the activated carbon particle, the set of the values of α, β and γ falls in the region of the limiting model. Furthermore, as verified in the last paragraph, the thermal effect can be neglected. Thus, for the toluene-activated carbon system, the external gas side mass transfer resistance is the controlling factor of the adsorption uptake rate.

4. Conclusions

An analytical solution for the mass diffusion in a spherical microporous solid suddenly exerted with a small step change of the gaseous phase adsorbate concentration is obtained. Both the thermal effect and external gas-side mass transfer resistance are considered. The solution can be used to evaluate the apparent solid-side mass diffusivity. In this analysis, it is found that the three factors α, β and γ govern the characteristics of the adsorption uptake curve. α and β are directly associated with the thermal effect and γ is related to the external gas-side mass transfer resistance. An adsorption system with a high value of α or a low value of β, the thermal effect can be neglected and the isothermal model will be appropriate to be used to predict the adsorption uptake curve. For a system with a high value of γ, the external gas-side mass transfer resistance will be small and the adsorbate concentration on the solid surface can be assumed to be in equilibrium with the ambient gas-side adsorbate concentration. In other words, the gas-side adsorbate concentration boundary layer can be ignored. The magnitude of γ is not only determined by the mass transfer Biot number ($B_{i,\,m}$) but also it is inversely proportional to the slope of the adsorption isotherms. Thus, for a system with steep adsorption isotherms, even the mass transfer Biot number is large, the external gas-side mass transfer resistance still cannot be neglected in the analysis.

The operating regions of four different models for predicting the adsorption uptake curve are summarized on a α/β versus γ diagram. For the value of γ exceeding 100, the external gas-side mass transfer resistance can be neglected. Furthermore, if the value of α/β exceeding 60, the simple isothermal model will be valid. The ratio, α/β, actually determines the importance of the thermal effect in an adsorption process. For the case with a high values of α/β, the thermal effect will be no longer important. However, the value of γ also affects the thermal effect. For the case with a higher value of γ, the thermal effect becomes relatively more important to the adsorption uptake curve. Thus, the value of α/β to reach the criterion for the isothermal model increases with the value of γ. From the result of this analysis, it can be foreseen that for the case with the value of γ much less than 0.1 the thermal effect can be completely ignored.

In this work the limiting solution for $D \rightarrow \infty$ is obtained. The limiting case considers the adsorbent as a lumped mass capacitance. For a fixed value of α and γ, the higher the value of β, the closer the solution toward that of the limiting case.

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