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Effect of Macropore Convection on Mass Transfer in a Bidisperse Adsorbent Particle

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Abstract. The importance of adsorption induced convection in the macropores of a bidisperse adsorbent particle is studied for a step change in mole fraction or total pressure at the surface of the particle. Material balance equations for a binary gas mixture are written for both the macropores and the micropores with allowance for convection in the macropores, which is described by Darcy's law. The coupled set of partial differential equations is solved by orthogonal collocation. The enhancement in mass transfer as a result of convection is assessed by comparing the fractional uptake curves obtained with and without allowance for convection. Both equilibrium-based and kinetic-based separation processes are considered. The effect of the presence of convection in determining the controlling diffusional resistance (macropore or micropore) is also examined. Due to inclusion of convection no single non-dimensional group alone can determine the relative importance of macropore and micropore resistances. Results show that convection can significantly affect the performance of an equilibrium-based macropore diffusion controlled process and that the enhancement in mass transfer is more for a particle with a high value of Darcy permeability.

Keywords: intraparticle convection, intraparticle mass transfer, pressure swing adsorption

Introduction

Manufacture of adsorbents like zeolites involves the agglomeration of crystals containing micropores into pellets by binders containing largely non-adsorbing macropores. Thus, these adsorbents have a bidisperse pore structure. Mass transfer through the macropores and micropores in these adsorbent particles can affect the performance of a pressure swing adsorption (PSA) process.

Ruckenstein et al. (1971) considered the problem of adsorption in solids with a bidisperse pore structure. They considered diffusional mass transfer in both the macropores and micropores. On the basis of this model, Ruckenstein et al. derived a general criterion to determine the controlling resistance in a bidisperse adsorbent particle. Ruthven and Loughlin (1972) modified this criterion for mass transfer in molecular sieves where the macropores have a negligible adsorption capacity. A number of theoretical models in the literature have made use of these criteria to neglect one of the two mass transfer resistances. This results in considerable mathematical simplification. For example, Farooq and Ruthven (1990), Hassan et al. (1986), Raghavan and Ruthven (1985), and Yang and Doong (1985) have assumed micropore resistance to be the controlling resistance in their models.

Convection can develop in the macropores of an adsorbent particle due to adsorption and desorption in the particle and due to the pressure gradients that exist as a result of pressurization and blowdown. Axial convection through adsorbent particles was considered by Lu et al. (1992a, 1992b) along with diffusional mass transfer mechanisms in the modeling of PSA processes using large pore adsorbents. Kruglov and Aris (1995) have introduced a convective flux into an analysis of adsorption kinetics. Recently, Taqvi and LeVan (1996) have studied the role of convection and diffusion in a large pore with adsorptive walls. Convection and pore (mutual) diffusion were considered in the gas phase and surface diffusion was considered in the adsorbed phase. The authors showed that when the component being considered was present in bulk and was not a trace component, the convective flux was as large as the diffusive flux, except when the limiting case of equimolar counterdiffusion was approached, and convection could significantly enhance mass transfer through the pore. Thus, convection will be important in processes like bulk separation of gases, natural gas storage, and adsorptive refrigeration.

This paper considers the effect of macropore convection on transport through a bidisperse adsorbent particle for a step change in concentration at the surface. The change in concentration is introduced by either changing the mole fraction at a constant pressure or by varying the total pressure at a fixed mole fraction. The model of the adsorbent particle that we have used is similar to that of Ruckenstein et al. We use Darcy's law to describe the convective flux inside the macropores of the particle. Dimensionless parameters are varied in the analysis to consider both macropore controlled processes as well as micropore controlled processes. In examples, we consider both equilibrium-based separations as well as kinetic-based separations for a binary gas mixture. Enhancement in mass transfer as a result of convection is studied by comparing the net uptake by the adsorbent particle in the presence and absence of convection. Parameter values are chosen and boundary conditions are applied in such a way that the adsorption induced convection can be isolated from the total convection arising due to both adsorption and pressure gradients. We also examine the effect of the presence of convection on the criteria proposed by Ruckenstein et al. and Ruthven and Loughlin for determining the controlling diffusional resistance in a bidisperse adsorbent particle.

Mathematical Model

Flux Equation

Pore diffusion, Knudsen diffusion, and convection can be important mass transfer mechanisms in the macropores of an adsorbent particle. Knudsen diffusion is important only if the pore radius is very small or the operating pressure is very low. For light gases the diffusion coefficient is on the order of 10^{-5} m^2/s. If an adsorption process involving gases with molecular weights of about 30 is carried out near atmospheric pressure and 298 K, then a Knudsen coefficient of about 10^{-5} m^2/s corresponds to a macropore radius on the order of 100 nm. In this pore, mutual diffusion and Knudsen diffusion would be of equal importance. For bidisperse adsorbent particles with macropore radii much larger than 100 nm, such as many pelletized adsorbents, Knudsen diffusion can be neglected.

In the absence of Knudsen diffusion, the flux of component A in the gas phase of a macropore is given by

$$N_A = -D_{AB} c \frac{\partial y_A}{\partial r} + y_A (N_A + N_B) \tag{1}$$

where the diffusion coefficient D_{AB} has an effective value, i.e., $D_{AB} = D'_{AB}\chi/\tau_p$ where D'_{AB} is the bulk gas-phase diffusion coefficient, χ is the particle porosity, and τ_p is the particle tortuosity. Sometimes, Knudsen diffusion is incorporated into Eq. (1) in an approximate way by replacing D_{AB} by $(D_{AB_{\mathrm{eff}}})_A$ which is given by the Bosanquet equation (Scott and Dullien, 1962)

$$\frac{1}{(D_{AB_{\mathrm{eff}}})_A} = \frac{1}{D_{AB}} + \frac{1}{K_A} \tag{2}$$

where K_A is the Knudsen diffusion coefficient.

Assuming ideal gas behavior and isothermal conditions, bulk flow can be described by the Darcy's law expression

$$N_A + N_B = -\frac{CP}{\mu RT}\frac{\partial P}{\partial r} \tag{3}$$

Combining Eqs. (1) and (3), the fluxes for components A and B are given by

$$N_A = -\frac{D_{AB}P}{RT}\frac{\partial y_A}{\partial r} - \frac{CP}{\mu RT} y_A \frac{\partial P}{\partial r} \tag{4}$$

$$N_B = \frac{D_{AB}P}{RT}\frac{\partial y_A}{\partial r} - \frac{CP}{\mu RT}(1 - y_A)\frac{\partial P}{\partial r} \tag{5}$$

The binary diffusion coefficient is inversely proportional to pressure under conditions of interest, so we have

$$D_{AB} = D_{AB_{\mathrm{ref}}}\frac{P_{\mathrm{ref}}}{P} \tag{6}$$

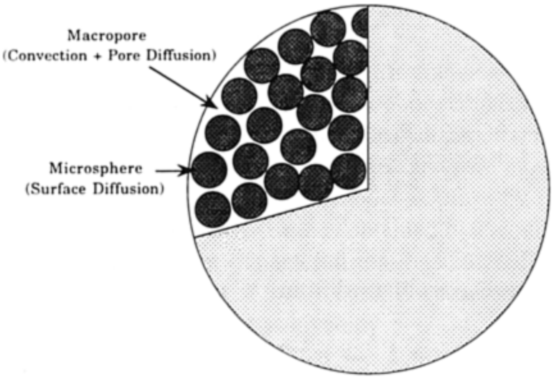

Figure 1. Schematic diagram of an adsorbent particle.

Material Balance Equations

Similar to the model of Ruckenstein et al. (1971), we have assumed the adsorbent particle to consist of a spherical macroporous structure containing spherical microporous structures (microspheres), as shown in Fig. 1. We assume that significant adsorption takes place only inside the microspheres.

Inside the macropores, a material balance is written assuming that the gas transport mechanism is comprised of Darcy convection and gas-phase pore diffusion (or a combination of gas-phase and Knudsen diffusion following Eq. (2)). Inside the microspheres, a material balance on the solid phase is written assuming that the components move only by surface diffusion or micropore diffusion. Material balances on component A and on both components for the macropores are

$$\chi\frac{y_A}{RT}\frac{\partial P}{\partial t} + \chi\frac{P}{RT}\frac{\partial y_A}{\partial t} + (1-\chi)\frac{3D_A}{r_c}\left.\frac{\partial q_A}{\partial r_m}\right|_{r_m=r_c} + \frac{1}{r^2}\frac{\partial(r^2 N_A)}{\partial r} = 0 \tag{7}$$

$$\frac{\chi}{RT}\frac{\partial P}{\partial t} + (1-\chi)\frac{3D_A}{r_c}\left.\frac{\partial q_A}{\partial r_m}\right|_{r=r_c} + (1-\chi)\frac{3D_B}{r_c}\left.\frac{\partial q_B}{\partial r_m}\right|_{r_m=r_c} + \frac{1}{r^2}\frac{\partial(r^2(N_A+N_B))}{\partial r} = 0 \tag{8}$$

Here, r_m is the radial coordinate for the microsphere, r_c is the radius of the microspheres, and D_A is the diffusion coefficient of component A in the microspheres. For boundary conditions, at the center of the particle, a no flux condition is imposed. At the outer boundary, different boundary conditions can be applied to study different cases.

To keep the problem simple, it is assumed that both components follow the linear isotherm

$$q_i = k_i c_i \tag{9}$$

where k_i is the linear isotherm constant for component i and c_i is the molar concentration of component i. As a result of this assumption the micropore diffusion coefficients of the two components can be treated as constants and independent of each other.

The material balances on the microspheres are

$$\frac{\partial q_A}{\partial t} = \frac{D_A}{r_m^2}\frac{\partial}{\partial r_m}\left(r_m^2\frac{\partial q_A}{\partial r_m}\right) \tag{10}$$

$$\frac{\partial q_B}{\partial t} = \frac{D_B}{r_m^2}\frac{\partial}{\partial r_m}\left(r_m^2\frac{\partial q_B}{\partial r_m}\right) \tag{11}$$

For boundary conditions, at the center of a microsphere the adsorbed-phase flux is zero, and at the surface of the microsphere q_A is related to P and y_A by an adsorption isotherm.

Non-dimensional variables for this system of equations are

$$\begin{aligned} N_A^* &\equiv N_A RT r_p / D_{AB_{\text{ref}}} P_{\text{ref}} \\ P^* &\equiv P/P_{\text{ref}} \\ q_A^* &\equiv q_A/q_{A_{\text{ref}}} \\ \tau &\equiv D_{AB_{\text{ref}}} t / r_p^2 \\ r^* &\equiv r/r_p \\ r_m^* &\equiv r_m/r_c \end{aligned}$$

where r_p is the radius of the adsorbent particle. Also, we have the parameters

$$\begin{aligned} \Lambda_A &\equiv q_{A_{\text{ref}}} RT / y_{A_{\text{ref}}} P_{\text{ref}} \\ C^* &\equiv C P_{\text{ref}} / D_{AB_{\text{ref}}} \mu \end{aligned}$$

where Λ_A is the partition ratio for component A and C^* characterizes the convective flow relative to the diffusive flow in the macropores. For a linear isotherm, Λ_i equals k_i.

In figures which follow, τ is a variable. It is interesting to know its order of magnitude compared to the actual time t. For an adsorbent particle of radius 3 mm and a mutual diffusivity of 10^{-5} m^2/s, τ and t have the same order of magnitude. In other words, if t is equal to 1 s, then $\tau \approx 1$.

Non-dimensional equations are

$$N_A^* = -\frac{\partial y_A}{\partial r^*} - C^* P^* y_A \frac{\partial P^*}{\partial r^*} \qquad (12)$$

$$N_A^* + N_B^* = -C^* P^* \frac{\partial P^*}{\partial r^*} \qquad (13)$$

$$\chi y_A \frac{\partial P^*}{\partial \tau} + \chi P^* \frac{\partial y_A}{\partial \tau} + (1-\chi)\Lambda_A \frac{3D_A/r_c^2}{D_{AB_{\text{ref}}}/r_p^2} \times \left.\frac{\partial q_A^*}{\partial r_m^*}\right|_{r_m^*=1} + \frac{1}{r^{*2}} \frac{\partial (r^{*2} N_A^*)}{\partial r^*} = 0 \qquad (14)$$

$$\chi \frac{\partial P^*}{\partial \tau} + (1-\chi)\Lambda_A \frac{3D_A/r_c^2}{D_{AB_{\text{ref}}}/r_p^2} \left.\frac{\partial q_A^*}{\partial r_m^*}\right|_{r_m^*=1} + (1-\chi)\Lambda_B \frac{D_B}{D_A} \frac{3D_A/r_c^2}{D_{AB_{\text{ref}}}/r_p^2} \left.\frac{\partial q_B^*}{\partial r_m^*}\right|_{r_m^*=1} + \frac{1}{r^{*2}} \frac{\partial (r^{*2}(N_A^* + N_B^*))}{\partial r^*} = 0 \qquad (15)$$

$$\frac{\partial q_A^*}{\partial \tau} = \frac{D_A/r_c^2}{D_{AB_{\text{ref}}}/r_p^2} \frac{1}{r_m^{*2}} \frac{\partial}{\partial r_m^*} \left(r_m^{*2} \frac{\partial q_A^*}{\partial r_m^*} \right) \qquad (16)$$

$$\frac{\partial q_B^*}{\partial \tau} = \frac{D_B}{D_A} \frac{D_A/r_c^2}{D_{AB_{\text{ref}}}/r_p^2} \frac{1}{r_m^{*2}} \frac{\partial}{\partial r_m^*} \left(r_m^{*2} \frac{\partial q_B^*}{\partial r_m^*} \right) \qquad (17)$$

Some interesting ratios of parameters arise naturally in the non-dimensional equations. D_A/D_B represents the ratio of micropore diffusion coefficients of A and B and Λ_A/Λ_B represents the capacity of the adsorbent to adsorb component A relative to component B.

Absence of Convection

Ruckenstein et al. (1971) considered only diffusional mass transfer mechanisms in the macropores and microspheres of a bidisperse adsorbent particle and obtained an analytical solution for a step change in concentration. Linear adsorption isotherms, constant diffusion coefficients, and adsorption by both macropores and microspheres were the other major assumptions made in their model. Ruthven and Loughlin (1972) simplified the solution obtained by Ruckenstein et al. for zeolites and other similar adsorbents where adsorption in the macropores is negligible and the adsorbate in the microspheres can be treated as a single adsorbed phase. For our problem, their solution is

$$\frac{c_A - c_{Ai}}{c_{Af} - c_{Ai}} = 1 + \frac{4\pi}{3\beta r^*} \sum_{k=1}^{\infty} \sum_{q=1}^{\infty} \frac{k(-1)^k \sin(k\pi r^*) \exp(-\alpha \xi_{qk}^2 \tau)}{\xi_{qk}^2 \left[\cot^2 \xi_{qk} - \left(1 - \frac{k^2\pi^2}{3\beta}\right) \frac{1}{\xi_{qk}^2}\right]} \qquad (18)$$

where ξ_{qk} is obtained from

$$\xi_{qk} \cot \xi_{qk} = 1 - k^2\pi^2/3\beta \quad k = 1, 2, 3, \ldots, \infty \qquad (19)$$

For each value of k, there are an infinite number of roots of the above equation. In Eq. (18), $\alpha = (D_A/r_c^2)/(D_{AB}/r_p^2)$ and $\beta = (1-\chi)\alpha\, dq_A/dc_A$. β represents the ratio of time constants for micropore and macropore diffusion and is obtained by equating the macropore transport rate to the microsphere transport rate in the adsorbent particle. On the basis of their model, Ruthven and Loughlin proposed the following criterion for determining the controlling resistance in a bidisperse particle:

if $\beta < 10^{-2}$, micropore resistance controls
if $10^{-2} < \beta < 10^3$, both resistances compete
if $\beta > 10^3$, macropore resistance controls

As mentioned earlier, when modeling an adsorbent particle it is generally assumed that micropore diffusion controls the adsorption process inside the particle. Inclusion of convection results in a parallel mechanism of mass transfer in the macropores with the micropore mass transfer being unaffected. Thus, even though convection enhances overall mass transfer in the particle, inclusion of convection would have a negligible effect on a micropore controlled process. However, for a process in the transition regime or the macropore control regime, a large convective flux can reduce the importance of the macropore diffusional resistance.

Problem and Method of Solution

We assume that the adsorbent particle is initially in equilibrium with the gas phase and that a step change in concentration is introduced at the particle surface either by varying the gas-phase mole fraction while the total pressure outside the particle remains constant or by changing the total pressure while the bulk gas-phase mole fraction remains constant.

To study the enhancement in mass transfer in the adsorbent particle as a result of macropore convection, we compare the uptake by the particle at different times when convection is not taken into account (the model of Ruckenstein et al.) and our model. Uptake by the adsorbent particle at any time is obtained by calculating the total amount of material that has entered the particle since the start of the process. For example, for component A the uptake is given by

$$M_t = \int_0^t 4\pi r_p^2 N_A \big|_{r=r_p} dt \tag{20}$$

In the absence of convection, the fractional uptake by the particle is

$$\frac{M_t}{M_\infty} = \frac{\displaystyle\sum_{k=1}^{\infty}\sum_{q=1}^{\infty} \frac{k^2\left[1 - \exp\left(-\alpha\xi_{qk}^2\tau\right)\right]}{\xi_{qk}^4\left[1 + \cot^2\xi_{qk} - \left(1 - \frac{k^2\pi^2}{3\beta}\right)\frac{1}{\xi_{qk}^2}\right]}}{\displaystyle\sum_{k=1}^{\infty}\sum_{q=1}^{\infty} \frac{k^2}{\xi_{qk}^4\left[1 + \cot^2\xi_{qk} - \left(1 - \frac{k^2\pi^2}{3\beta}\right)\frac{1}{\xi_{qk}^2}\right]}} \tag{21}$$

Thus, the fractional uptake in the absence of convection depends only on the parameters α and β and is independent of the magnitude of the change in concentration at the surface of the particle or the initial value of the concentration.

We have solved the partial differential equations in our model by orthogonal collocation. At each collocation point an ordinary differential equation with time as the independent variable is written resulting in a set of ordinary differential equations. Jacobi polynomials are used to obtain collocation points inside the macroporous structure as well as the microspheres. The polynomials are of the form

$$f(r^*) = A_0 + \sum_{i=1}^{\infty} A_i u^i \tag{22}$$

where $u = r^{*2}$. The built-in feature of this polynomial approximation is that it satisfies $(\partial f/\partial r^*)|_{r^*=0} = 0$. Hence, the boundary conditions that the first derivatives of pressure and mole fraction with respect to radial distance at the center of the macroporous structure and the microspheres are zero are automatically satisfied. Collocation points were located at zeros of the Jacobi polynomial $p^{(1,0.5)}(u)$. We used 25 interior collocation points for macropores and 5 for microspheres. The set of ordinary differential equations in time was solved using the Gear's method solver LSODE (1980) to obtain the mole fraction and pressure profiles inside the particle. Solutions were obtained for both equilibrium-based separation and kinetic-based separation with different values of β to include both macropore controlled processes and micropore controlled processes. Net uptake was calculated by numerically integrating the total flux at the boundary of the particle. While comparing the fractional uptake obtained from our model with the uptake obtained from the model of Ruckenstein et al., the change in concentration is introduced by changing the mole fraction rather than the pressure so that the diffusion coefficient remains constant in our model and a fair comparison can be made with the model of Ruckenstein et al.

Results

Equilibrium-Based Separation

In an equilibrium-based separation, it is the difference in the capacity of the adsorbent to adsorb different gases in different amounts that causes the separation. Typically, the adsorbent has a high adsorption capacity for one of the components in the separation of a binary mixture. Taqvi and LeVan (1996) observed a strong dependence of the convective flux on the adsorptive capacity of the adsorbent. Thus, we expect a significant enhancement in the uptake by the particle for a macropore controlled equilibrium-based process.

Micropore Limitation. We first consider a micropore controlled equilibrium-based separation with $\Lambda_A = 1000$, $\Lambda_B = 10$, $(D_A/r_c^2)/(D_B/r_c^2) = 1$, $C^* = 10^4$, and $\alpha = 2 \times 10^{-5}$. Thus, for this case β is 0.01. Values of Darcy permeability for several systems have been measured by Allawi and Gunn (1987). In dimensionless form, C^* can range in value from 0.1 to 10^4. We have used a large value of C^* to ensure negligible pressure gradients inside the particle. Thus, any increase in uptake would be due to adsorption induced convection. We have considered an increase in mole fraction at the particle surface from 0.2 to 0.8. Figure 2 shows the fractional uptake by the particle obtained from Eq. (21) when convection is not taken into account and the uptake obtained from using our model. As expected, inclusion of convection has a negligible effect on the uptake curve.

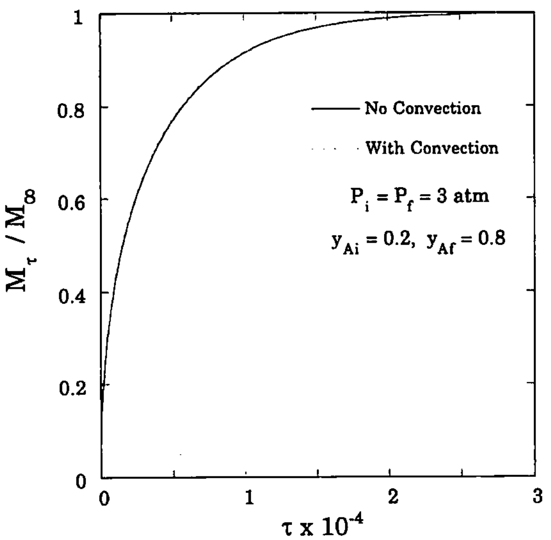

Figure 2. Fractional uptake of component A by the adsorbent particle for $\Lambda_A = 10^3$, $\Lambda_A/\Lambda_B = 10^2$, $C^* = 10^4$, $(D_A/r_c^2)/(D_B/r_c^2) = 1$, $\alpha = 2 \times 10^{-5}$ and $\beta = 0.01$.

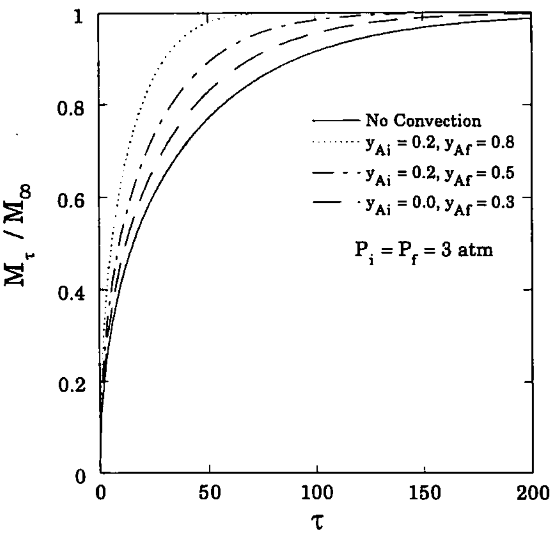

Figure 3. Fractional uptake of component A by the adsorbent particle for $\Lambda_A = 10^3$, $\Lambda_A/\Lambda_B = 10^2$, $C^* = 10^4$, $(D_A/r_c^2)/(D_B/r_c^2) = 1$, $\alpha = 2$ and $\beta = 1000$.

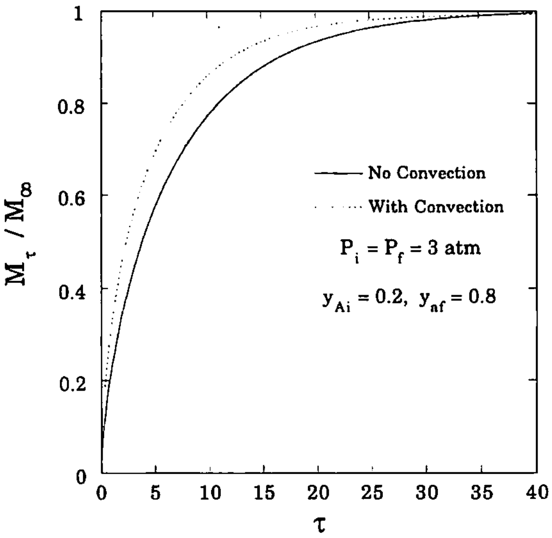

Figure 4. Fractional uptake of component A by the adsorbent particle for $\Lambda_A = 100$, $\Lambda_A/\Lambda_B = 1$, $C^* = 10^4$, $(D_A/r_c^2)/(D_B/r_c^2) = 100$, $\alpha = 0.02$ and $\beta = 1$.

Macropore Limitation. In order to simulate a macropore controlled process, a value of 2 is used for α and values of other parameters are unchanged. This results in a value of $\beta = 1000$. The uptake curve obtained from Eq. (21) is shown in Fig. 3. For our model, the convective flux depends on the initial value of the concentration and the size of the step change introduced at the surface. Uptake curves for the different cases considered are also shown in Fig. 3. For the same initial value of the mole fraction of component A, $y_{Ai} = 0.2$, the uptake by the particle was larger at any time and the adsorption capacity was reached more quickly for a larger step change ($y_{Af} = 0.8$) compared to a smaller step change ($y_{Af} = 0.5$). When the size of the step change was the same ($y_{Af} - y_{Ai} = 0.3$) but the initial value of the mole fraction was zero, the enhancement in mass transfer due to convection was less than when y_{Ai} was 0.2.

Kinetic-Based Separation

In a kinetic-based separation, separation occurs because one gas diffuses faster than the other in the adsorbed phase inside the micropore structure. Thus, a kinetic-based separation process cannot be macropore controlled. At most, the value of β can lie in the transition regime where both resistances are important. The fractional uptake curves obtained for a typical kinetic-based separation process are shown in Fig. 4 for $\beta = 1$. We assume $\Lambda_A = 100$, $\Lambda_B = 100$, $(D_A/r_c^2)/(D_B/r_c^2) = 100$, $C^* = 10^4$, and $\alpha = 0.02$. We have considered a large increase in surface concentration from $y_{Ai} = 0.2$ to $y_{Af} = 0.8$. The increase in the fractional uptake due to convection is considerably less in this case even for such a large increase in the surface mole fraction in comparison to the equilibrium-based separation considered earlier. This can be attributed to the fact that the partition ratio is smaller, hence the magnitude of the induced convective flux is smaller.

Step Change in Total Pressure

For the cases that we have considered so far, the step change in concentration was introduced by varying the mole fraction rather than the total pressure and the Darcy permeability was assumed to be very large to ensure negligible pressure gradients and a constant macropore diffusion coefficient. Thus, the increases in the particle uptake that were observed were due to adsorption induced convection only.

Convection can also arise as a result of pressure gradients that exist when the adsorbent particle is exposed to pressure variations at the boundary such as during pressurization and blowdown steps of a PSA cycle. Pressure gradients inside the particle are inversely related to the particle permeability. We study the effect of variation in the particle permeability on the uptake by the particle. The case we have considered is the macropore controlled equilibrium-based separation for which we found the largest increase in the uptake as a result of convection. We assume that the particle is initially in equilibrium at one atmosphere and the total pressure is raised to 3 atmospheres instantaneously. Thus, for this case considerable pressure gradients can exist and gas will be drawn in by convection to balance the pressure as well as to account for adsorption in the microspheres. We let $\Lambda_A = 1000$, $\Lambda_B = 10$, $(D_A/r_c^2)/(D_B/r_c^2) = 1$, $\alpha = 2$, and $\beta = 1000$. Figure 5(a) shows the fractional uptake curves for C^* equal to 0.1, 1, and 10^4. The corresponding pressure profiles inside the particle are shown in Figs. 5(b)–(d), respectively. Large pressure gradients exist in the macropores for $C^* = 0.1$. On increasing the permeability, the pressure inside the particle approaches the equilibrium value quickly. This results in a large adsorption induced convective flux and higher uptake by the particle at any time. Thus, the adsorption induced convective flux exceeds the convective flux that develops to balance the pressure in the particle.

Determining the Controlling Diffusional Resistance

The criterion proposed by Ruthven and Loughlin (1972) can be altered for the case when the contribution of macropore convection to mass transfer in the particle is significant. A large convective flux can move a transition regime process, where both diffusional resistances are important, to the micropore controlled regime. Similarly, for a macropore controlled process, if the convective flux increases the macropore mass transfer rate considerably, the micropore resistance can also become relevant.

In Fig. 6 we have plotted the fractional uptake by the adsorbent particle for an equilibrium-based separation for a step change in mole fraction at the surface from 0.2 to 0.8 both in the presence and absence of convection. We have assumed $\Lambda_A = 1000$, $\Lambda_B = 10$, $(D_A/r_c^2)/(D_B/r_c^2) = 1$, $C^* = 10^4$, and $\alpha = 2 \times 10^{-2}$. Thus, for this process $\beta = 10$, and the process falls in the transition regime where both resistances are important. As a result of convection in the macropores, the uptake by the particle obtained from our model is more than the fractional uptake obtained from Eq. (21). For the same conditions, we assume that the macropore diffusion coefficient increases by a factor of 1000 so that α and β change to 2×10^{-5} and 0.01, respectively. The fractional uptake by the particle for this case obtained from Eq. (21) is also shown in Fig. 6. Since time is made dimensionless with respect to the macropore diffusion time, we divided the time at which the uptake was obtained for this case by 1000 to plot the uptake curve on the same figure. It becomes evident from this figure that the increase in mass transfer due to convection for a transition regime process diminishes the importance of the macropore resistance and moves the process towards the micropore controlled regime.

Discussion

For a binary gas mixture, the ratio of convective flux to diffusive flux was written by Taqvi and LeVan (1996) as

$$\frac{\text{Convective Flux of } A}{\text{Diffusive Flux of } A} = \frac{y_A(N_A + N_B)}{(1 - y_A)N_A - y_A N_B} \tag{23}$$

For $y_A < 0.1$, the convective flux is less than 15% of the diffusive flux. Thus, convection is negligible for purification processes and the criterion of Ruthven and Loughlin (1972) can be used for determining the controlling diffusional resistance. For $y_A > 0.5$, the convective flux is greater than the diffusive flux for $N_A \gg N_B$. For equilibrium-based separation processes with $\Lambda_A \gg \Lambda_B$, we expect $N_A \gg N_B$.

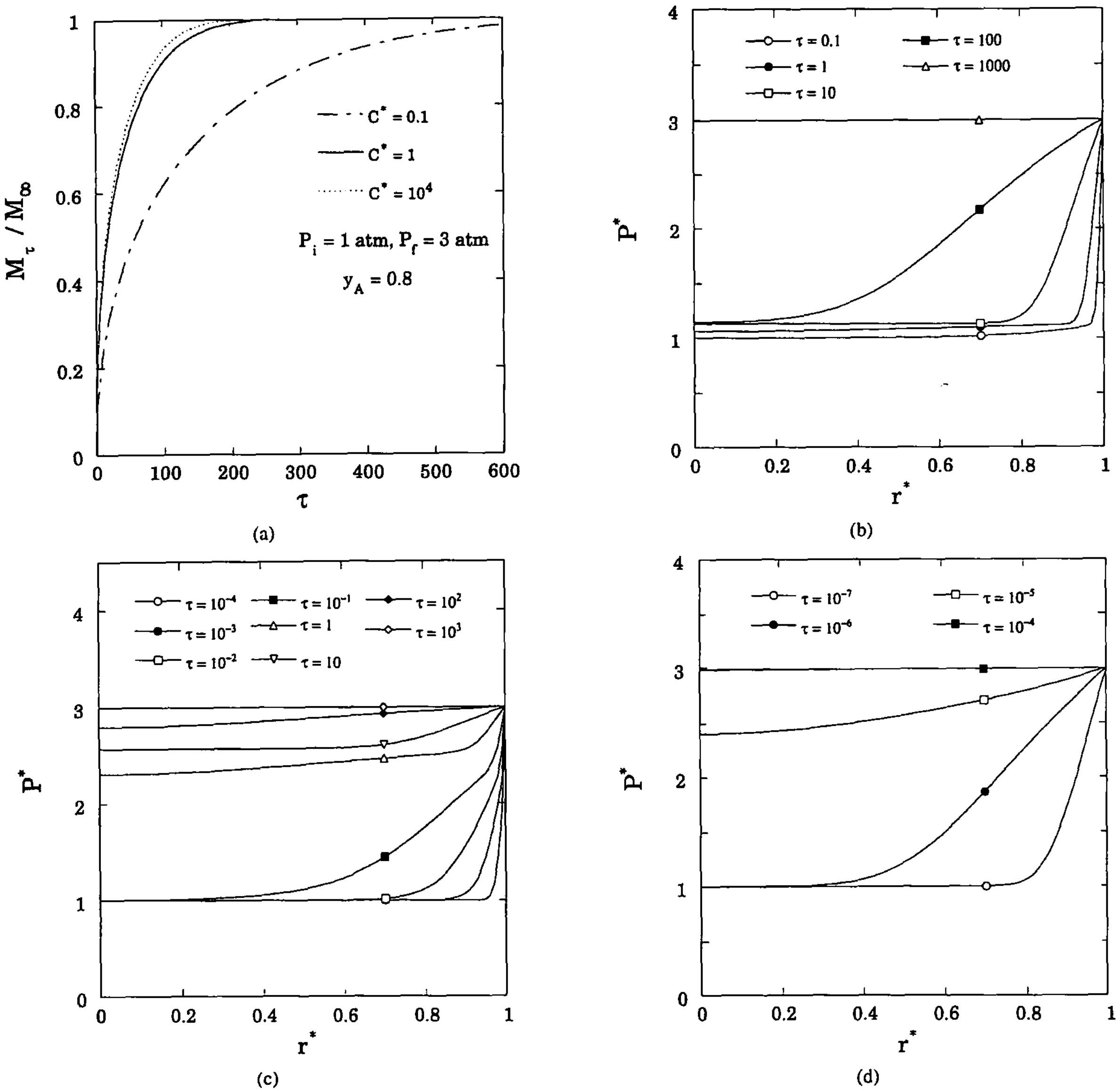

Figure 5. (a) Fractional uptake of component A by the adsorbent particle for $\Lambda_A = 10^3$, $\Lambda_A/\Lambda_B = 10^2$, $(D_A/r_c^2)/(D_B/r_c^2) = 1$, $\alpha = 2$ and $\beta = 1000$, (b) Pressure profiles for $C^* = 0.1$, (c) Pressure profiles for $C^* = 1$, (d) Pressure profiles for $C^* = 10^4$.

Therefore, for separation processes where adsorbent particles are exposed to mole fractions greater than 0.5, convection plays a dominant role in the macropores. A criterion ignoring convection is likely to overestimate the importance of macropore diffusion for such processes and the process may be micropore controlled even for large values of β. When $0.1 < y_A < 0.5$, the convective flux is not as large as the diffusive flux but still makes a significant contribution to mass transfer in the macropores. This would increase the relative importance of the micropore resistance and the values of β used for marking the boundaries between micropore, transition, and macropore regimes would be higher. For accurate predictions of the uptake by the particle, the complete model with allowance for convection should be used.

In our analysis we have considered the adsorption isotherm to be linear. For a nonlinear favorable isotherm, the enhancement in mass transfer by convection would be less at high pressures as the adsorption capacity of the adsorbent would not increase much due to an increase in the gas-phase concentration.

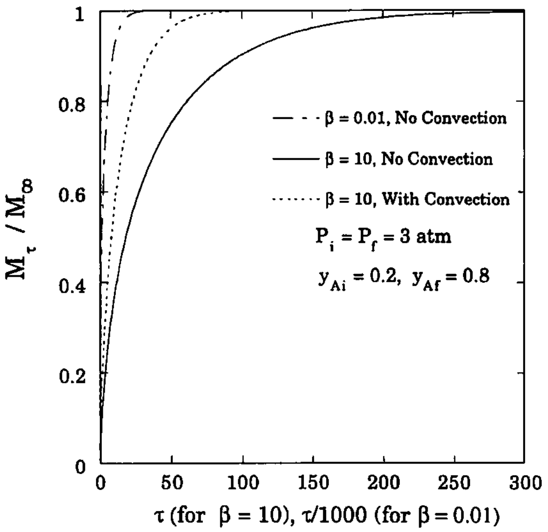

Figure 6. Fractional uptake of component A by the adsorbent particle for $\Lambda_A = 10^3$, $\Lambda_A/\Lambda_B = 10^2$, $C^* = 10^4$, $(D_A/r_c^2)/(D_B/r_c^2) = 1$.

An example of a process where macropore convection is important is the bulk separation of an equimolar hydrogen-methane mixture considered by Doong and Yang (1987). These authors found the micropore resistance to be dominant for values of β in the range of 0.1 to 10. The criterion of Ruthven and Loughlin (1972) predicts both macropore and micropore diffusional resistances to be equally important for these values of β. Doong and Yang attributed this anomaly to the presence of convection during the pressure changing steps. As our analysis shows, convection can also be present after pressurization as a result of adsorption in the microspheres. In the model of Doong and Yang, repressurization with the light product (hydrogen) is followed by a high pressure feed. Thus, the adsorbent particles are exposed to large changes in mole fraction at the surface which would generate a large convective flux in the macropores and reduce the importance of macropore diffusion. Hence, the presence of convection both during and after the pressure changing steps may account for the experimental observations of Doong and Yang.

Conclusions

We have developed a mathematical model to study mass transfer in a bidisperse adsorbent particle. Convection and pore diffusion are accounted for in the macropores and surface diffusion is considered in the micropores.

Enhancement in mass transfer in the adsorbent particle is observed as a result of convection in the macropores induced by adsorption in the micropores. The importance of macropore convection is assessed by studying the increase in the net uptake by the adsorbent particle when allowance is made for convection. The effect of convection is negligible for micropore diffusion controlled processes, as would be expected. For macropore diffusion controlled processes or processes that fall in the transition regime, the increase in uptake due to convection increases with an increase in the partition ratio, the change in concentration that the surface of the particle is exposed to, and the actual value of the concentration.

The enhancement in mass transfer by convection is directly related to the adsorption capacity of the adsorbent. Thus, when the partition ratio is very large or the particle is exposed to large changes in concentration at the surface, the magnitude of the induced convective flux is large. For an equilibrium-based separation, where the partition ratio is large, the enhancement in the particle uptake was much more than for a kinetic-based separation, where the partition ratio is typically smaller. Also, for a particle with a high permeability, because the equilibrium pressure is reached quickly, the adsorption induced convective flux in the macropores is large and results in a fast uptake by the particle.

The convective flux of any component is proportional to its mole fraction. For the same change in surface concentration, the increase in uptake was found to be more for the case where the initial concentration in the particle was larger. Therefore, enhancement in particle mass transfer can be large for a macropore controlled equilibrium-based process used for bulk gas separation.

A criterion that ignores convection for determining the controlling mass transfer resistance in a bidisperse adsorbent particle can overestimate the importance of macropore diffusional resistance for separation processes. For such processes, convection is the dominant mass transfer mechanism in the macropores at high mole fractions and the micropore resistance can be the controlling resistance in the regime where the criterion might predict both macropore and micropore resistances to be equally important.

Notation

Symbol	Definition
Arabic Symbols	
C	Darcy's coefficient of convective flow, m^2
c	concentration, mol/m^3 gas
D	diffusion coefficient in micropore or macropore, m^2/s
K	Knudsen diffusion coefficient, m^2/s
k	linear isotherm coefficient, m^3 gas/m^3 microspheres
N	flux in macropores, mol/m^2 s
P	pressure, Pa
q	adsorbed-phase concentration, mol/m^3 microspheres
R	gas constant, J/mol K
r	radius, m
T	temperature, K
t	time, s
y	mole fraction
Greek Symbols	
χ	porosity of an adsorbent particle
Λ	partition ratio
μ	viscosity of gas, kg/m s
τ	dimensionless time
τ_p	particle tortuosity
Subscripts	
A, B, i	components A, B, i
m	micropore

References

Allawi, Z.M. and D.J. Gunn, "Flow and Diffusion of Gases Through Porous Substrates," *A.I.Ch.E. J.*, **33**, 766–775 (1987).

Doong, S.J. and R.T. Yang, "Bidisperse Pore Diffusion Model for Zeolite Pressure Swing Adsorption," *A.I.Ch.E. J.*, **33**, 1045–1049 (1987).

Farooq, S. and D.M. Ruthven, "Numerical Simulation of a Kinetically Controlled Pressure Swing Adsorption Bulk Separation Process Based on a Diffusion Model," *Chem. Engng. Sci.*, **46**, 2213–2224 (1990).

Hassan, M.M., D.M. Ruthven, and N.S. Raghavan, "Air Separation by Pressure Swing Adsorption on a Carbon Molecular Sieve," *Chem. Engng. Sci.*, **41**, 1333–1343 (1986).

Hindmarsh, A.C., LSODE and LSODI, "Two New Initial-Value Ordinary Differential Equation Solvers," *ACM-SIGNUM Newsletter*, **15**(4), 10–11 (1980).

Kruglov, A. and R. Aris, "Adsorption Kinetics for the Case of Step and S-Shaped Isotherm," *A.I.Ch.E. J.*, **41**, 2395–2398 (1995).

Lu, Z., J.M. Loureiro, M.D. LeVan, and A.E. Rodrigues, "Intraparticle Convection Effect on Pressurization and Blowdown of Adsorbers," *A.I.Ch.E. J.*, **38**, 857–867 (1992a).

Lu, Z., J.M. Loureiro, M.D. LeVan, and A.E. Rodrigues, "Effect of Intraparticle Forced Convection on Gas Desorption from Fixed Beds Containing "Large-Pore" Adsorbents," *Ind. Engng. Chem. Res.*, **31**, 1530–1540 (1992b).

Raghavan, N.S. and D.M. Ruthven, "Pressure Swing Adsorption: Part III: Numerical Simulation of a Kinetically Controlled Bulk Gas Separation," *A.I.Ch.E. J.*, **31**, 2017–2025 (1985).

Ruckenstein, E., A.S. Vaidyanathan, and G.R. Youngquist, "Sorption by Solids with Bidisperse Pore Structures," *Chem. Engng. Sci.*, **26**, 1305–1318 (1971).

Ruthven, D.M. and K.F. Loughlin, "The Diffusional Resistance of Molecular Sieve Pellets," *Can. J. Chem. Eng.*, **50**, 550–552 (1972).

Scott, D.S. and F.A.L. Dullien, "Diffusion of Ideal Gases in Capillaries and Porous Solids," *A.I.Ch.E. J.*, **8**, 113–117 (1962).

Taqvi, S.M. and M.D. LeVan, "Role of Convection and Diffusion in a Single Pore with Adsorptive Walls," *Adsorption*, **2**, 299–309 (1996).

Yang, R.T. and S.J. Doong, "Gas Separation by Pressure Swing Adsorption: A Pore-Diffusion Model for Bulk Separation," *A.I.Ch.E.J.*, **31**, 1829–1842 (1985).