Direct Measurement of External Mass Transfer in Packed Sorbent Beds

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Numerous studies have measured the mass transfer coefficients at the fluid/particle interface in packed beds. The accumulated data has been presented both as empirical correlations (Upadhyay and Tripathi, 1975) and as supporting evidence for models of the basic mass transfer processes (Carberry, 1960; Kataoka et al., 1972). Most data has been obtained by the dissolution of uniform, geometric particles in an appropriate solvent; usually benzoic acid spheres in water. The exceptions are those studies by Moison and O'Hern (1959) and Selke et al. (1956) using ion exchange resins. Moison and O'Hern calculated j_D values from the breakthrough curve of a deep bed where external diffusion was the dominant mass transfer resistance. In contrast Selke and co-workers used a shallow bed technique. However, unlike the earlier work by Boyd et al. (1947), the effect of the fluid phase concentration gradient within the bed was incorporated into the analysis. Unfortunately only an approximate solution, based on small concentration gradients, was developed for estimating the mass transfer coefficient from the "initial" breakthrough (Bieber et al., 1954). The exact solution is presented below.

No single equation correlates the solid dissolution data over both the high and low Reynolds number regimes (Upadhyay and Tripathi, 1975; Kataoka et al., 1972). In particular, in the range $10 < Re' < 100$ there appears to be a change in the Reynolds number dependence of j_D. This uncertainty is compounded by the scatter in the accumulated data, with some experimental j_D values deviating by a factor of two from those given by the correlation equations. Moison and O'Hern (1959) concluded that both sets of ion exchange data were consistent with the solid dissolution data. However, comparison of Figure 16 in Moison and O'Hern (1959) with Figure 1 in Selke et al. (1956) shows that the different definitions of j_D and Re were not accounted for when combining the two sets of data. In fact, the best fit equation through the data of Selke and co-workers gives j_D values 70% higher than those based on the solid dissolution equations. This may be due to an underestimation of the ion counterdiffusivities as discussed in Selke et al. (1956).

Clearly estimates of the external mass transfer coefficient in packed beds using the existing correlations may be subject to considerable error. This problem is compounded by the errors associated with the estimation of the solute diffusivity and the effective mass transfer area of the particles, especially for irregular shaped particles. However these problems are overcome by direct measurement of the number of external, mass transfer units, N_e; thus, eliminating the need to know k_e and A_p separately. This technique is illustrated below.

THEORY

The normalized, material balance equation for a fixed bed adsorption column and the rate equation for mass transfer near the liquid-solid interface are given below:

$$\left(\frac{\partial X}{\partial \theta}\right)_Z + \frac{\Lambda}{\epsilon_b}\left(\frac{\partial Y}{\partial \theta}\right)_Z + \left(\frac{\partial X}{\partial Z}\right)_\theta = \frac{1}{\mathrm{Pe}}\left(\frac{\partial^2 X}{\partial Z^2}\right)_\theta \tag{1}$$

$$\frac{\Lambda}{\epsilon_b}\left(\frac{\partial Y}{\partial \theta}\right)_Z = \left(\frac{k_e A_p}{F}\right)(X - X^*) \tag{2}$$

Initially the fluid phase concentration at the particle surface, X^*, is zero. Thus, Eqs. 1 and 2 can be combined to give:

$$\frac{1}{\mathrm{Pe}}\left(\frac{\partial^2 X}{\partial Z^2}\right)_\theta - \left(\frac{\partial X}{\partial Z}\right)_\theta - N_e X - \left(\frac{\partial X}{\partial \theta}\right)_Z = 0 \tag{3}$$

where N_e is the number of external mass transfer units ($= k_e A_p/F$). If the variation of X with θ is small, Eq. 3 reduces to a second order, ordinary differential equation whose solution for $Z = 1$, i.e., at the exit of the bed, is:

$$X_b = e^{-N_e'} \tag{4}$$

with

$$N_e' = \frac{\mathrm{Pe}}{2}\left(\left(1 + \frac{4N_e}{\mathrm{Pe}}\right)^{1/2} - 1\right)$$

When axial dispersion in the bed is negligible, the modified number of mass transfer units, N_e', reduces to N_e. The restriction that $(\partial X/\partial\theta)_Z$ be negligible is satisfied if the solute distribution ratio, Λ, is very large. Note Eq. 4 is independent of the shape of the adsorption isotherm. Dunlop et al. (1976) and Cooney et al. (1978) derived Eq. 4 by integrating the rate equation (Eq. 2) over the length of the packed bed. However this less rigorous formulation ignores the possible effects of axial dispersion and the concentration gradient $(\partial X/\partial\theta)_Z$.

The value of X_b is found by plotting X versus θ and extrapolating back to $\theta = 1$. The achievement of an "initial" breakthrough, i.e., a non zero value of X_b, does not require a shallow bed in the sense of Selke et al. (1956). On the contrary, very deep beds will exhibit an initial breakthrough provided the flow rate is sufficiently large to cause N_e to be less than about 5.

EXPERIMENTAL

Materials

The adsorbent was Norit RB-2, an activated carbon extruded in the form of cylindrical pellets with a uniform diameter of 2 mm. The pellets were sorted according to length and those used in the experiments ranged in length from 0.64 to 0.48 mm. This corresponds to an equivalent spherical

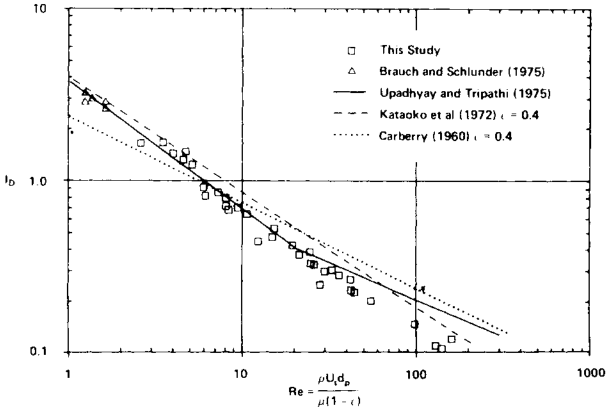

Figure 1. j_D vs. R_e' correlation.

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TABLE 1. RESULTS OF THE EXPERIMENT.

Run No*	X_b	N_e	Sc	j_D	R_e'
A1	0.090	2.57	849	0.70	8.15
A2	0.095	2.51	845	0.69	8.23
A3	0.090	2.57	1086	0.83	7.30
A4	0.090	2.57	1095	0.83	7.16
A5	0.155	1.96	1033	0.62	11.1
A6	0.205	1.66	1033	0.52	15.1
A7	0.260	1.40	1000	0.43	12.6
A8	0.125	2.20	924	0.64	9.50
A9	0.075	2.78	882	0.79	8.03
A10	0.070	2.86	882	0.82	6.00
B1	0.140	2.20	832	1.24	5.35
B2	0.095	2.70	803	1.46	4.76
B3	0.100	2.63	706	1.31	4.64
B4	0.085	2.84	741	1.43	4.03
B5	0.060	3.31	730	1.64	3.55
B6	0.065	3.20	721	1.62	2.62
B7	0.200	1.77	716	0.91	5.95
B8	0.550	0.62	915	0.39	24.5
B9	0.625	0.48	915	0.30	29.1
B10	0.625	0.48	915	0.30	33.2
B11	0.645	0.45	936	0.29	35.9
B12	0.655	0.43	915	0.27	42.0
B13	0.700	0.36	915	0.23	42.2
C1	0.740	0.31	1084	0.22	53.9
C2	0.500	0.72	997	0.48	15.0
C3	0.540	0.64	959	0.41	19.2
C4	0.585	0.55	985	0.37	21.4
C5	0.615	0.50	965	0.32	25.0
C6	0.620	0.49	965	0.32	26.0
C7	0.690	0.38	965	0.25	28.1
C8	0.740	0.31	926	0.19	54.5
D1	0.585	0.54	915	0.14	97.9
D2	0.645	0.45	902	0.115	162
D3	0.670	0.40	911	0.107	130
D4	0.690	0.38	911	0.100	139

* Run A, Column ID = 36.6 mm; L = 234 mm; Pe = 35
Run B, Column ID = 36.6 mm; L - 106 mm; Pe = 16
Run C, Column ID = 19.1 mm; L = 108 mm; Pe = 16
Run D, Column ID = 12.1= mm; L = 254 mm; Pe variable 43 to 52
Note: All runs @ c_0 equals 0.62 mM/L except for runs A9 to B6 where c_0 equals 0.31 mM/L and B6 and B7 where c_0 equals 1.25 mM/L.

diameter, based on the specific particle area, of 2.6 mm. The adsorbate was analytical grade sodium salicylate dissolved in distilled water. Inlet concentrations of 1.25, 0.62 and 0.31 mM/L were used.

Method

Packed beds of various heights of the activated carbon were formed in the upper portion of perspex columns 36.6 mm and 19.1 mm ID and 500 mm long. The lower portion of the column was filled with inert glass beads (2mm diameter). The salicylate solution entered the bottom of the column under gravity feed. The flow rate was measured with a rotameter upstream of the column. The temperature of the solution, both entering and leaving the column, was measured by thermometer to the nearest 0.2°C. The effluent flow for each run was collected in either 5 or 10 cm^3 increments. The salicylate concentrations were measured using a Unicam 1800 spectrophotometer.

RESULTS AND DISCUSSION

The results are presented in Table 1 and Figure 1. The Peclet numbers in Table 1 were estimated from Re′ and the bed height using the relationship developed in Miyauchi and Kiruchi (1975). The variation in Schmidt number reflects variations in the experimental temperature; from 17 to 26°C. Figure 1 also includes j_D values calculated from the data of Brauch and Schlunder (1975) using Eq. 4. For comparison the empirical equations presented by Upadhyay and Tripathi (1975) and the theoretical equations of Carberry (1960) and Kataoka et al. (1972) are shown in Figure 1. The only systematic deviation of the data from these curves is for $\mathrm{Re}' > 50$. However, even these data fall within the scatter band of the data correlated by Upadhyay and Tripathi (1975). As expected j_D is independent of inlet concentration.

The precision of this technique is largely dependent upon the exponential relationship between X_b and N_e. For a given absolute error in determining X_b the absolute error in N_e increases as X_b decreases. However, the corresponding percentage error in N_e is large for either large or small values of X_b. It is therefore desirable to use intermediate values of X_b; i.e., if all X_b can be measured to the nearest 0.02 then the percentage error in N_e will not exceed 10% provided $0.07 < X_b < 0.75$.

Dunlop et al. (1976), Cooney et al. (1978) and Radcliffe (1978) have all applied this technique to the analysis of hemoperfusion columns, in which the external mass transfer resistance is performance limiting. Here k_e is composed of a fluid phase and a membrane phase resistance; the latter resulting from the thin protective coating of polymer placed around the adsorbent particles. However, both Dunlop et al. (1976) and Cooney et al. (1978) erroneously concluded that this latter resistance was in part due to the intraparticle (solid) resistance. This stemmed from the assumption that k_e was in fact the overall (fluid plus solid phase) mass transfer coefficient. However, if the fluid phase concentration at the particle surface, X^*, is zero then there can be no intraparticle resistance at that stage.

In conclusion, this technique provides a direct means of measuring the number of external mass transfer units in adsorption or ion exchange columns, without the need to know either the effective mass transfer area of the particles or the solute diffusivity. Further the results in Figure 1 represent an independent confirmation of the existing mass transfer data measured by solid dissolution and ion exchange in deep beds.

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NOTATION

A_p = effective external particle area
c = liquid phase concentration
D_a = axial dispersion coefficient
d_p = equivalent particle diameter
F = volumetric flow rate
j_D = mass transfer j factor
k_e = external mass transfer coefficient
L = length of bed
N_e' = number of external mass transfer units (Eq. 4)
Pe = Peclet number (= U_sL/D_a)
q = solid phase concentration
R_e' = modified Reynolds number (= $\rho U_s d_p/\mu(1 - \epsilon)$)
U_s = superficial velocity
t = time
$\bar{t}$ = mean residence time
X = dimensionless fluid phase conc. (= c/c_0)
Y = dimensionless solid phase conc. (= q/q_0)
Z = dimensionless length co-ordinate

Greek Letters

ϵ = bed porosity
θ = dimensionless time ($= t/\bar{t}$)
μ = fluid viscosity
ρ = fluid or bed density
Λ = distribution parameter ($= \rho_b q_0 / c_0$)

Subscripts

b = bed, breakthrough
0 = normalizing or input value

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Holdup Correlations in Slurry-Solid Fluidized Beds

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The use of slurry-solids fluid beds plays an important role in the development of synthetic fuels and the hydrogen processing of petroleum resids. In the H-Coal process in particular, coal oil slurries are processed over extrudates of hydrodesulfurization catalyst. The objective of this note is to present a model which describes the volume fraction occupied by the slurry phase. The accurate prediction of the liquid holdup is important not only for the calculation of the bed height in liquid solid fluidized beds, but also is required for the development of a model predicting the holdup in three-phase fluidized beds.

Although several correlations have been considered in the literature (Richardson and Zaki, 1954; Ramamurthy and Sabbaraju, 1973) for pure liquids, very little has been published for slurry systems. The objective of this paper is to extend the work of previous investigators for systems of particular interest to the H-Coal process. A summary of correlations describing liquid-solid fluidized beds has been presented elsewhere (Vasalos et al., 1979, 1980).

In the present publication, the application of two correlations is considered: 1) the Richardson and Zaki; and 2) Ramamurthy and Sabbaraju. The first relates the liquid volume fraction (ϵ_l) due to bed expansion to the ratio of the superficial velocity (U_l) to the terminal velocity of a single particle (U_t):

$$\epsilon_l \eta = U_l / U_t \tag{1}$$

The second is based on an empirical approach where a function of Reynolds and Galileo numbers is related to the function $[1 - 1.21(1 - \epsilon_l)^{2/3}]^{-1}$. This function relates the velocity of a fluid in minimum cross-section of the bed to the superficial velocity. It is derived by assuming that the particles are arranged in an imaginary node of a simple cubical lattice.

EXPERIMENTAL

Data used in this work were obtained in a cold flow unit, details of which have been reported elsewhere (Vasalos et al., 1979). The unit consists of a glass reactor 15 cm in diameter and 5 m in height. Extrudates of hydrodesulfurization catalyst (1.8-mm diameter, 5.1-mm length) were fluidized with coal fines-kerosene slurries and mineral oil. The density and viscosity of these fluids are reported in Table 1. It has been found that this slurry has about the same viscosity as the H-Coal liquids at actual operating conditions.

For each set of conditions, the bed height was measured by scanning the entire reactor length with an elevator on which was mounted a 10 mc gamma-ray source and a detector. From the change in the gamma-ray absorption, the bed height can easily be inferred. The liquid or slurry holdup is then determined from the equation:

$$1 - \epsilon_l = M / \rho_c A H \tag{2}$$

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