MOMENT ANALYSIS OF CONCENTRATION DECAY IN A BATCH ADSORPTION VESSEL

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Moment equations are derived for concentration decay curves of tracer in a well-mixed batch slurry adsorber. This gives relations between the rate parameters for mass transfer and adsorption and the moments of the experimentally measurable curves. The results provide a method for measuring rate parameters in slurry systems. The method is illustrated by evaluating fluid-to-particle mass transfer coefficients and effective diffusivities from experimental data for the adsorption of dodecylbenzenesulfonate in slurries of bone char particles.

Introduction

Agitated vessels containing slurries of adsorbent or catalyst can be widely applied to the removal of pollutants and to reaction processes. However, overall performance can be seriously reduced by several mass transport resistances. This has led to a number of investigations of mass transport steps. Transport coefficient between bulk fluid and particle surfaces has been measured by use of adsorption, and a recent review with additional data is available^{2,4,8}.

Intraparticle diffusion might be another important resistance in slurries as well as in fixed-beds^{6,13}. In an earlier stage of the research in this area, an analytical solution was derived by neglecting mass transfer resistance at the external surface of particles¹. The effective diffusivity was evaluated by comparing the experimental result with the analytical solution³. External mass transfer resistance was taken into consideration in recent analyses⁷. Such analyses assume that the isotherm is linear.

The curve-fitting technique employed in these studies leads to some uncertainties in determining the parameters simultaneously from experimental results. The moment method, however, has shown a usefulness in the analysis of the data from dynamic testing in linear systems where plural rate parameters are included^{5,9,11,12}.

The present note shows that moment analysis is applicable to the reduced concentration decay curves for a batch adsorber. Theoretical equations for the moments are derived and then compared with the experimental results obtained from DBS-bone char

system where a considerable portion of the isotherm is regarded as linear.

Theory

Basic equations

It is assumed that mechanical agitation is sufficient to maintain uniform concentration of adsorbate and uniform distribution of suspended particles. The dynamic mass balances of adsorbate in liquid and particles are given as follows:

$$\frac{dC}{dt} = -k_f a_s (C - c_{r=R}) \quad (1)$$

$$D_e \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) - \beta \frac{\partial q}{\partial t} = \epsilon \frac{\partial c}{\partial t} \quad (2)$$

with initial conditions

$$C = C_0 \quad \text{at } t = 0 \quad (3)$$

$$c = 0 \quad \text{at } t = 0 \quad (4)$$

and with boundary conditions

$$k_f (C - c_{r=R}) = D_e \left(\frac{\partial c}{\partial r} \right)_{r=R} \quad (5)$$

$$\frac{\partial c}{\partial r} = 0 \quad \text{at } r = 0 \quad (6)$$

The particles are assumed to be spherical, of radius R . For linear reversible adsorption where the rate of adsorption is rapid enough with respect to mass transport steps, instantaneous equilibrium between the adsorbate at the pore wall surface and that within the pore space leads to the equation

$$\frac{\partial q}{\partial t} = K \frac{\partial c}{\partial t} \quad (7)$$

Solution in Laplace domain

Eqs. (1)~(7) are transformed into Laplace domain

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Fig. 1 Adsorption equilibrium isotherm of DBS on PS bone char

Table 1 Properties of bone chars PS-F1*

Original mesh*	#20/30
Bulk density*	0.58 g/cc
Particle density**	1.14 g/cc
Surface area***	91 m ² /g
Porosity****	0.62
Composition* [wt%]	
	Ca ₃ (PO ₄) ₂ 83
	Carbon 9.5
	CaCO ₃ 8.5
	Other minerals 0.2

* Supplied by the manufacturer.

** Determined by mercury displacement.

*** BET-Nitrogen area.

**** Calculated from particle density by assuming the true density to be 3.0.

and the concentration decay in liquid phase can be written as

$$\frac{\bar{C} - \bar{C}_\infty}{\bar{C}_0 - \bar{C}_\infty} = \frac{1 + \delta_0}{\delta_0} \left\{ \frac{1}{s + k_f a_s \Phi} - \frac{1}{s} \frac{1}{1 + \delta_0} \right\} \quad (8)$$

where

$$\Phi(s) = \frac{\phi_s - \tanh \phi_s}{\phi_s + (Bi - 1) \tanh \phi_s} \quad (9)$$

$$\phi_s = R \left[\frac{(\varepsilon + \rho K)}{D_e} s \right]^{1/2} \quad (10)$$

$$\delta_0 = (m_s / \rho)(\varepsilon + \rho K) \quad (11)$$

and

$$a_s = (m_s / \rho)(3/R) \quad (12)$$

Moments of decay curve

The moments of the concentration decay curve are related to Eq. (8) by the equation

$$\frac{\bar{C} - \bar{C}_\infty}{\bar{C}_0 - \bar{C}_\infty} = \mu_0 - \mu_1 s + \mu_2 \frac{s^2}{2!} - \mu_3 \frac{s^3}{3!} + \dots \quad (13)$$

where μ_n is defined as

$$\mu_n = \int_0^\infty \frac{\bar{C} - \bar{C}_\infty}{\bar{C}_0 - \bar{C}_\infty} t^n dt \quad (14)$$

Each moment can be obtained by expanding the right-hand side of Eq. (8) into Taylor's series of Laplace transform operator s . The zeroth and the first moment obtained thus are given as

$$\mu_0 = \frac{T_D}{15} \left(1 + \frac{5}{Bi} \right) \frac{1}{1 + \delta_0} \quad (15)$$

$$\mu_1 = \mu_0^2 + \frac{1}{525} T_D^2 \frac{1}{1 + \delta_0} \quad (16)$$

where

$$T_D = R^2 \frac{(\rho K + \varepsilon)}{D_e} \quad (17)$$

The steady-state equilibrium concentration is related to the adsorption equilibrium constant by

$$c_\infty / c_0 = 1 / (1 + \delta_0) \quad (18)$$

Then a measurement of the concentration with time, t , until the steady state is attained, provides sufficient data for evaluating k_f , D_e and K . This is because independent two-moment Eqs. (15) and (16) together with the steady-state Eq. (17) are given for the three unknown parameters.

Experimental

A Pyrex cylindrical adsorber (10 cm I.D., 15 cm high) was equipped with four stationary baffles of stainless steel along the circumference. Two-bladed solid impeller (2 cm high $\times$ 6 cm wide) was positioned so that it was located at about the middle of the liquid height. Details of the construction are given elsewhere¹⁴. The reactor was kept in a constant-temperature bath (30°C).

Dodecylbenzenesulfonate (DBS)-bone char system was chosen because of its linear equilibrium relation over a considerable range of solute concentration. This is shown in Fig. 1.

The impeller speed was fixed at 300 rpm, which gave a reasonably homogeneous suspension of the bone char particles of the maximum size adopted here (# 48/65).

The properties of the bone char particles supplied by the manufacturer (Naruto Chemical Co.) are summarized in Table 1. These particles were ground and screened.

One litre of 100 mg/l DBS aqueous solution was prepared and 0.40 gram (1.20 gram for Run A-2) of bone char particles was put into the vessel after boiling in distilled water to remove fine dust from the surface of the particles.

Experimental conditions used are listed in Table 2. Concentration in the vessel was determined from ultraviolet spectrophotometry with periodic sampling of about 1 cc from the 1 litre solution. The peak height resulting from the adsorption due to the existence of aromatic ring was high enough to determine with reasonable accuracy the concentrations during the runs.

Typical plots of $(C_0 - C_\infty) / (C - C_\infty)$ are given in Fig. 2. These plots for $(C - C_\infty) / (C_0 - C_\infty) \geq 0.005$ were then used to determine the moments from

Table 2 Experimental conditions and results

Run	Particle [mesh]	Average radius R [cm]	m_s [g/cc]	C_∞/C_0 [—]	μ_0 [hr]	μ_1 [hr ²]	T_D [hr]	D_e [cm ² /sec]	Bi	k_f [cm/sec]
A-1	48/65	0.0127	0.40×10^{-3}	0.70	2.68	10.57	50.4	2.9×10^{-7}	35.8	0.00083
A-2	48/65	0.0127	1.20×10^{-3}	0.43	1.51	4.15	48.0	3.1×10^{-7}	53.3	0.0013
B	80/100	0.00815	0.40×10^{-3}	0.70	1.15	1.88	22.2	2.8×10^{-7}	46.3	0.0016
C	100/150	0.0063	0.40×10^{-3}	0.70	0.57	0.516	12.0	2.9×10^{-7}	26.0	0.0012
D	150/200	0.0043	0.40×10^{-3}	0.70	0.36	0.178	5.8	3.0×10^{-7}	15.2	0.0011

Eq. (14) by computation. The results of the zeroth and first moments for each particle size are included in Table 2, where D_e and k_f calculated from Eqs. (15) and (16) are also shown.

The particle density, ρ , was determined to be 1.14 by mercury displacement in a glass pycnometer, and then the porosity of the particle, ε , was estimated to be 0.62 by assuming true density to be 3.0.

The equilibrium parameter, δ_0 , calculated from C/C_0 gave $K=288$ cc/g, which corresponds to the dotted line in Fig. 1.

Discussion

The effective diffusivity obtained in the present investigation appeared to be of reasonable order of magnitude in comparison with the previous results of D_e , $0.9 \sim 5.9 \times 10^{-7}$ cm²/sec, obtained from adsorption of DBS on several different kinds of activated carbons¹³. In those cases, the isotherms were strongly nonlinear so that the rectangular isotherm model was assumed to be valid.

The film transport coefficients, k_f , evaluated in Table 2 appeared nearly independent of particle size. This tendency agreed well with several previous results^{2,4} for particles of larger diameter than $100 \mu^{10}$. However, contradictory results were given by Huang and Li⁷. Their data showed a clear dependency of k_f on particle size for ion exchange resin-aqueous solution system, where the small density difference and thus the small relative velocity between the particles and the surrounding fluid may justify this result.

The evaluation procedure of the effective diffusivity, proposed by Huang⁷, was based upon the analytical solution for diffusion from a stirred vessel of limited volume. The film mass transfer coefficient obtained from the initial slope of the concentration decay curve would be rather prone to error. However, the present method provides two independent equations, Eqs. (15) and (16), which permit the simultaneous evaluation of intraparticle diffusivity and film coefficient.

The application of moment analysis to a slurry adsorber with continuous, steady feed and effluent and adsorbent particles which are suspended and retained

Fig. 2 Plots of $(C - C_\infty)/(C_0 - C_\infty)$ versus time

within the vessel has been proposed, and the mass transfer coefficients from bulk liquid to particles were evaluated experimentally⁵. However, important information concerning the intraparticle mass transport is contained in the intractable tailing part of the response curve, especially in the case involving considerably large adsorption equilibrium constant and slow intraparticle diffusivity, which is often met in liquid-phase adsorption.

The present method is advantageous in the cases where transport processes of large time constants are involved.

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Nomenclature

a_s	= outer surface area of particles per unit volume of particle free liquid	[cm ⁻¹]
Bi	= Biot number, $k_f R/D_e$	[—]
C	= bulk concentration of adsorbate in liquid phase in adsorber	[g/cm ³]
C_0	= initial concentration of adsorbate	[g/cm ³]
C_∞	= steady-state concentration in liquid	[g/cm ³]
$\bar{C}(s)$	= Laplace transform of $C(t)$	
c	= concentration in a particle	[g/cm ³]

D_e	= effective intraparticle diffusivity based upon cross sectional area of particle	[cm ² /sec]
K	= adsorption equilibrium constant	[cm ³ /g]
k_f	= fluid to particle mass transfer coefficient	[cm/sec]
m_s	= particle concentration	[g/(cm ³ of particle free liquid)]
q	= amount adsorbed in particle	[g/g]
R	= radius of particle	[cm]
r	= radial distance from center of particle	[cm]
s	= transform variable	[sec ⁻¹]
T_D	= time constant of diffusion with simultaneous adsorption defined by Eq. (16)	[sec]
t	= time	[sec]
δ_0	= ratio of adsorption capacity of particle to liquid, defined by Eq. (11)	[—]
ε	= void fraction in particle	[—]
μ_n	= n -th moment	[sec ^{n}]
ρ	= density of particle	[g/cm ³]
ϕ_s	= dynamic Thiele's modulus defined by Eq. (10)	
Φ	= function defined by Eq. (9)	

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LIQUID-LIQUID EXTRACTION IN A MULTISTAGE VIBRATING DISK COLUMN

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Mass transfer characteristics of a multistage vibrating disk column are studied for the extraction of methyl isobutyl ketone-acetic acid-water system.

The disk vibration definitely increases the mass transfer rate, and in the high vibration range the over-all mass transfer capacity coefficient becomes nearly three times that in the absence of disk vibration.

The increase in mass transfer rate by disk vibration is mainly caused by the increase in dispersed-phase holdup and the decrease in droplet size, and the resulting remarkable increase in interfacial area.

Introduction

When agitation is provided to a multistage vibrating disk column (MVDC) by vibrating the disks or perforated plates, the disk vibration is expected to promote mass transfer between phases of a gas-liquid or liquid-liquid system in the column. A violent disk vibration, however, will also increase the axial mixing in the column, which in turn may lower the overall

mass transfer efficiency of the column. Therefore, mass transfer characteristic must be fully studied to operate the MVDC properly.

The authors studied the mass transfer characteristics of a MVDC for a case of concurrent gas-liquid contacting operation in connection with the axial mixing characteristics of the column⁷⁾.

In this paper, mass transfer characteristics of the MVDC are discussed for a counter-current liquid-liquid extraction operation and an increase in the extraction efficiency due to disk vibration is interpreted in terms of the drop size and the holdup of the

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