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Effect of Particle Size Distributions on the Moments of Adsorption Uptakes or Chromatographic Elution Curves

吸着の平衡到達率曲線またはクロマトグラフ流出曲線のモーメントに対する粒径分布の影響

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Moment analysis is used to determine adsorption rate constants from adsorption uptake curves of batch adsorption or chromatographic elution curves. Frequently, particles employed for adsorption studies have size distributions and then the effect of particle size distribution on the moment analysis may become significant when the intraparticle phenomena are rate-controlling. Six typical size distributions are employed in this note to examine the relation between the parameters involved in distribution curves and the parameters determined from moment analysis. First, the moments of adsorption uptake curves are derived for batch adsorption on adsorbent particles having a size distribution. The moments of chromatographic elution curve are also given for the same case. Secondly, parameters included in the moment expressions are related to the size distribution parameters for normal, log-normal, rectangular, symmetrical triangular, Rosin-Rammler and Gaudin–Schumann distribution.

Uptake of Batch Adsorption Measurement

Mass balance of adsorbate in batch adsorption for particles of size distribution $f(R)$ on volume fraction basis are given as follows:

$$\frac{dC}{dt} = -\int_0^\infty a_s N(R) f(R) dR \tag{1}$$

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

with initial and boundary conditions

$$\left.\begin{array}{ll} C = C_0,\ q = 0,\ M_t = 0 & at\ \ t = 0 \\ C = C_\infty,\ q = K^* C_\infty,\ M_t = M_\infty & at\ \ t = \infty \end{array}\right\} \tag{3}$$

$$N(R) = \rho_P \cdot D \frac{\partial q}{\partial r}\Big|_{r=R} \tag{4}$$

$$C = \frac{q\,|_{r=R}}{K^*} \tag{5}$$

Solution of adsorption uptake in Laplace domain is obtained in a similar manner as Ref. (3), (4) and (6).

$$\overline{1 - \frac{M_t}{M_\infty}} = \frac{1+\delta_0}{\delta_0} \times \left\{ \frac{1}{p + \int_0^\infty \Phi(R, p) f(R) d(R)} - \frac{1}{p(1+\delta_0)} \right\} \tag{6}$$

$$\left.\begin{array}{l} \Phi(R, p) = a_s \dfrac{\rho_P K^* D}{R} \{\phi \coth\phi - 1\} \\ \phi = R\sqrt{\dfrac{p}{D}} \\ \delta_0 = m_s K^* \left(= \dfrac{C_0 - C_\infty}{C_\infty}\right) \\ a_s = \dfrac{m_s}{\rho_P} \cdot \dfrac{3}{R} \left(= \dfrac{S}{W}\right) \end{array}\right\} \tag{7}$$

The moments are related to the solution in Laplace domain as follows:

$$\mu_n = \lim_{p \to 0} \left(-\frac{d}{dp}\right)^n \left(\overline{1 - \frac{M_t}{M_\infty}}\right) \tag{8}$$

Then the moments of adsorption uptakes are

$$\mu_0 = \frac{1}{(1+\delta_0)} \cdot \frac{\overline{R}^2}{15D} \cdot F_2 \tag{9}$$

$$\mu_1 = \mu_0^2 + \frac{1}{(1+\delta_0)} \cdot \frac{\overline{R}^4}{525 D^2} \cdot F_t \tag{10}$$

where

$$F_t = \frac{10}{3} F_4 - \frac{7}{3} (F_2)^2 \tag{11}$$

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$$F_2 = \frac{1}{\overline{R}^2}\int_0^\infty R^2 f(R)\,dR \tag{12}$$

$$F_4 = \frac{1}{\overline{R}^4}\int_0^\infty R^4 f(R)\,dR \tag{13}$$

These F_t, F_2 and F_4 are the parameters determined from the size distribution.

Chromatography

In the case of the chromatographic elution curve, the first moment is not affected by the particle size distribution[2]. The second central moment for the system having the particle size distribution is given by Dougharty[2]

$$\mu_2' = \frac{2z}{u}\cdot\frac{E_z}{u^2}\left\{1+\frac{(1-\varepsilon)}{\varepsilon}(\varepsilon_a+\rho_P K^*)\right\}^2 + \frac{2z}{u}\cdot\frac{(1-\varepsilon)}{\varepsilon}\cdot\frac{(\varepsilon_a+\rho_P K^*)^2\overline{R}^2}{15D_a}\cdot F_2 \tag{14}$$

where F_2 is a factor due to size distribution and is given by Eq. (12)

Parameters F_2 and F_t for typical size distributions

In Table I, F_2 and F_t corresponding to the possible size distributions are shown. Normal and log-normal distributions are the most common ones met in the commertial adsorbent particles. Rectangular and triangular distributions are employed for the sake of simplicity. Rosin-Rammler and Gaudin-Schumann distributions are met when particles are prepared by grinding.

Extention to bi-disperse pore structure

The moments of adsorption uptakes in the case of bidispersed pore structure of adsorbent and size distribution of the microparticles are given as follows[5]:

$$\mu_0 = \frac{1}{(1+\delta_0)(\varepsilon_a+\rho_P K^*)} \times\left\{\frac{\rho_P K^*\overline{a}^2}{15D}\cdot F_2' + \frac{R^2}{15D_a}(\varepsilon_a+\rho_P K^*)^2\right\} \tag{15}$$

$$\mu_1 = \mu_0^2 + \frac{1}{(1+\delta_0)}\left[\frac{\rho_P K^*}{(\varepsilon_a+\rho_P K^*)}\cdot\frac{2}{315}\left(\frac{\overline{a}^2}{D}\right)^2 \cdot F_4' - \frac{(\rho_P K^*)^2}{(\varepsilon_a+\rho_P K^*)^2}\cdot\left(\frac{\overline{a}^2}{15D}\right)^2\cdot(F_2')^2 + \frac{1}{525}\left(\frac{R^2}{D_a}\right)^2(\varepsilon_a+\rho_P K^*)^2\right] \tag{16}$$

where

$$F_2' = \frac{1}{\overline{a}^2}\int_0^\infty a^2 f(a)\,da \tag{17}$$

$$F_4' = \frac{1}{\overline{a}^4}\int_0^\infty a^4 f(a)\,da \tag{18}$$

and D and D_a are, respectively, diffusivity in micropore and in macropore. If macroporocity $\varepsilon_a \ll \rho_P K^*$, then Eq. (16) reduces to

$$\mu_1 = \mu_0^2 + \frac{1}{(1+\delta_0)}\cdot\frac{1}{525} \times\left[\left(\frac{\overline{a}^2}{D}\right)^2 F_t' + \left(\frac{R^2}{D_a}\right)^2(\rho_p K^*)^2\right] \tag{16'}$$

where F_t' is the same form as Eq. (11).

The second central moment of chromatographic elution curve for the same case is derived elsewhere[1]. The term for micropore diffusion is found there to be multiplied by F_2'. as follows:

$$\frac{2z}{u}\cdot\frac{(1-\varepsilon)}{\varepsilon}\cdot\frac{\rho_P K^*\overline{a}^2}{15D}\cdot F_2'$$

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Notation

a = radius of micro-particle [cm]
$\overline{a}$ = average radius of micro-particle [cm]
a_s = outer surface area of particles per unit volume of fluid phase [cm²/cc]
C = bulk concentration of adsorbate in fluid phase [mol/cc]
C_0 = initial bulk concentration of adsorbate [mol/cc]
C_∞ = steady-state bulk concentration [mol/cc]
D = intraparticle diffusivity based on amount adsorbed gradient driving force [cm²/sec]
D_a = effective intraparticle diffusivity [cm²/sec]
E_z = axial dispersion coefficient based on void space in the bed [cm²/sec]
F_2 = defined by Eq. (12) [−]
F_4 = defined by Eq. (13) [−]
F_t = defined by Eq. (11) [−]
$f(R)$ = distribution function of the particle radii on volume fraction basis [−]
K^* = adsorption equilibrium constant [cc/g]
k = relative width of rectangular distribution [−]
M_t = total amount adsorbed at time t [mol]
M_∞ = total amount adsorbed at equilibrium [mol]
m = relative width of triangular distribution [−]

Table I Parameters F_2 and F_t for typical size distributions

pattern	distributin function $f(R)$	parameter	first moment of distribution	second central moment of distribution	F_2	F_t
normal	$\frac{1}{\sigma_N\sqrt{2\pi}}\exp\left[-\frac{(R-R_{N0})^2}{2\sigma_N^2}\right]$	$s\left(=\frac{\sigma_N}{R_{N0}}\right)$	R_{N0}	σ_N^2	$1+s^2$	$1+\frac{46}{3}s^2+\frac{23}{3}s^4$
log-normal	$\frac{1}{R}\cdot\frac{1}{\sigma_L\sqrt{2\pi}}\cdot\exp\left[-\frac{(\ln R-\ln R_{L0})^2}{2\sigma_L^2}\right]$	σ_L	$R_{L0}\exp\left(\frac{\sigma_L^2}{2}\right)$	$\overline{R}^2\left\{\exp(\sigma_L^2)-1\right\}$	$\exp(\sigma_L^2)$	$\frac{10}{3}\exp(6\sigma_L^2)-\frac{7}{3}\exp(2\sigma_L^2)$
rectangular	0 for $R<(1-k)\overline{R}$, $(1+k)\overline{R}<R$ $\frac{1}{2k\overline{R}}$ for $(1-k)\overline{R}\leq R\leq(1+k)\overline{R}$	k $(0<k\leq 1)$	$\overline{R}$	$\frac{\overline{R}^2k^2}{3}$	$1+\frac{k^3}{3}$	$1+\frac{46}{9}k^2+\frac{11}{27}k^4$
symmetrical triangular	0 for $R<(1-m)\overline{R}$, $(1+m)\overline{R}<R$ $\frac{R}{m^2\overline{R}^2}-\frac{1}{m^2\overline{R}}+\frac{1}{m\overline{R}}$ for $(1-m)\overline{R}\leq R\leq\overline{R}$ $-\frac{R}{m^2\overline{R}^2}+\frac{1}{m^2\overline{R}}+\frac{1}{m\overline{R}}$ for $\overline{R}\leq R\leq(1+m)\overline{R}$	m $(0<m\leq 1)$	$\overline{R}$	$\frac{\overline{R}^2m^2}{6}$	$1+\frac{m^2}{6}$	$1+\frac{23}{9}m^2+\frac{17}{108}m^4$
Rosin-Rammler	$-\frac{d}{dR}\{\exp(-bR^n)$	b & n	$\frac{1}{b^{1/n}}\cdot\frac{1}{n}\Gamma\left(\frac{1}{n}\right)$	$\frac{1}{b^{2/n}}\left[\frac{2}{n}\Gamma\left(\frac{2}{n}\right)-\frac{1}{n^2}\left\{\Gamma\left(\frac{1}{n}\right)\right\}^2\right]$	$2n\Gamma\left(\frac{2}{n}\right)/\left\{\Gamma\left(\frac{1}{n}\right)\right\}^2$	$\left[\frac{10}{3}\cdot\frac{4}{n}\Gamma\left(\frac{4}{n}\right)-\frac{7}{3}\cdot\frac{4}{n^2}\times\left\{\Gamma\left(\frac{2}{n}\right)\right\}^2\right]/\frac{1}{n^4}\left\{\Gamma\left(\frac{1}{n}\right)\right\}^4$
Gaudin-Schumann	$\frac{d}{dR}\left(\frac{R}{R_{max}}\right)^n$	R_{max} & n	$\frac{n}{n+1}\cdot R_m$	$R_m^2\left\{\frac{n}{n+2}-\frac{n^2}{(n+1)^2}\right\}$	$\frac{(n+1)^2}{n(n+2)}$	$\frac{(n+1)^4}{n^4}\left\{\frac{10}{3}\cdot\frac{n}{(n+4)}-\frac{7}{3}\cdot\frac{n^2}{(n+2)^2}\right\}$

m_s = mass of adsorbent per unit volume of fluid phase [g / cc]

$N(R)$ = mass flux at the external surface of particles of radius R [mol / cm^2 sec]

p = transform variable [sec^{-1}]

q = amount adsorbed [mol /g]

R = radius of particle [cm]

$\bar{R}$ = average radius [cm] $= \int_0^\infty Rf(R)dR / \int_0^\infty f(R)dR$

R_{L0} = radius at the peak for log-normal distribution [cm]

R_{N0} = radius at the peak for normal distribution [cm]

r = radial position in a particle [cm]

S = total surface area of particles [–]

s = (σ_N / R_{N0}) [–]

t = time [sec]

u = interstitial velocity of fluid [cm/sec]

W = volume of the fluid phase [cc]

z = longitudinal position in bed [cm]

Greek symbols

δ_0 = ratio of total amount adsorbed to total amount remained in the fluid phase at equilibrium [–]

ε = void fraction in the bed [–]

ε_a = void fraction in the particle or in the macro - particle [–]

μ_0 = zeroth moment [sec]

μ_1 = first moment [sec^2]

μ_2' = second central moment [sec^2]

ρ_P = particle density [g / cc]

σ_N = standard deviation of normal distribution [–]

σ_L = standard deviation of log - normal distribution [–]

Φ = defined by Eq. (7) [–]

ϕ = defined by Eq. (7) [–]

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