tion is proposed which when used in association with a theoretical laminar flow model enables the required sterilizer length to be determined.

NOTATION

a = constant parameter in Equation (3)
A = frequency factor
b = constant parameter in Equation (3)
c = constant parameter in Equation (3)
C_0 = inlet spore or nutrient concentration
$<C>$ = bulk spore or nutrient concentration
ΔE = activation energy
k = rate coefficient for spore inactivation or nutrient denaturation
L = sterilizer length
n = pseudoplastic index
R = dimensionless radial coordinate
R_g = gas constant
T = temperature
u = local velocity
$<u>$ = bulk velocity, 10 cm/s

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The Prediction of Desorption Times for Fixed-Bed Adsorbers

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The problem of designing fixed-bed adsorption processes reduces, in effect, to the prediction of the breakthrough and regeneration curves for a packed adsorption column. In most practical systems, the adsorption step is carried out under conditions such that the equilibrium isotherm is highly favorable (type I of the Brunauer classification). For such nonlinear systems, exact mathematical analysis of the column response is difficult and time consuming (see, for example, Zwiebel, Gariepy, and Schnitzer, 1972; Garg and Ruthven, 1973, 1974*b*). For the adsorption cycle, however, constant pattern behavior is almost always achieved under practical operating conditions, and a sufficiently accurate prediction of the breakthrough curve may therefore be obtained simply from the equilibrium capacity and the constant pattern profile. Theoretical calculation of the constant pattern profile is straightforward, since this only requires the integration of the appropriate kinetic rate equation, subject to the boundary condition imposed by the equilibrium isotherm (see, for example, Hall, Eagleton, Acrivos, and Vermeulen, 1966; Fleck, Kirwan, and Hall, 1973). Alternatively, the spread of the constant pattern profile may be determined directly by experiment, and the dynamic adsorption capacity may then be estimated from the equilibrium capacity and the length of the mass transfer zone (length of unused bed), as outlined by Hersh (1961).

No such simple approximation is available for the desorption or regeneration cycle since, if the equilibrium relationship is favorable for adsorption, it will always be unfavorable for desorption. This is true even if the temperature is raised during the desorption cycle. At sufficiently high temperatures, the isotherm will approach linearity, but the curvature will not normally be reversed. The limiting form of the desorption profile will therefore be of the proportionate pattern type. Since desorption is generally the rate limiting step in a cyclic operation (Chi and Lee, 1969), the development of a simple method for predicting the desorption time is of considerable practical importance.

For most design purposes, it is not necessary to know the entire form of the desorption curve. Rather, the design engineer needs only to be able to predict the time, or the volume of the desorbing fluid, required to reduce the effluent concentration of the adsorbate to some arbitrarily chosen value close to zero. The slope of a type I isotherm increases continuously as the concentration decreases. The

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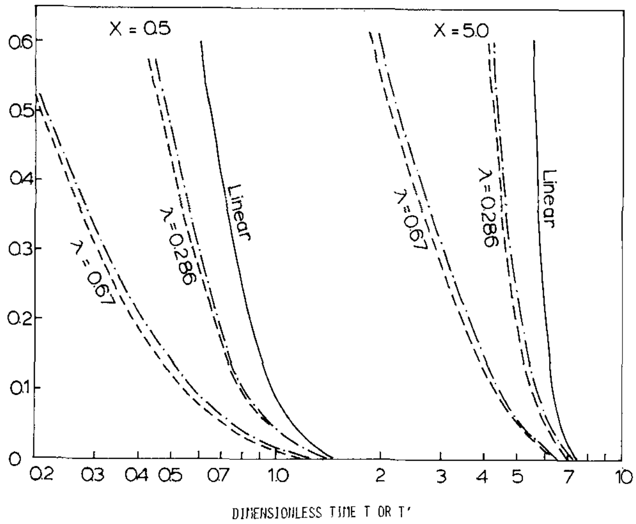

Fig. 1. Comparison of theoretical desorption curves from nonlinear systems, calculated from the analysis of Garg and Ruthven (1973, 1974) with the curves for a linear system with the same dimensionless column length (X or X'). (Curves for macropore control, – – –; curves for micropore control, —·—·; linear solution, ———.)

desorption curve for such a system will therefore approach asymptotically the curve for a linear system, with equilibrium constant equal to the limiting slope of the isotherm at zero concentration (the Henry's law constant). This is illustrated in Figure 1 in which the desorption curves calculated numerically from the full solution of the differential equations, integrated over the column length (Garg and Ruthven, 1973, 1974*b*), are compared with the curves calculated from the linear analysis of Rosen (1952, 1954). At high sorbate concentrations, the curves for the nonlinear systems show considerable deviation, but it is evident that the limiting time required for desorption may be estimated reasonably well from the simple linear model. This method of predicting the limiting desorption time from the asymptotic linear solution should be applicable even to nonisothermal desorption processes, provided that the temperature at the column outlet always either increases or remains constant during the desorption cycle since, under these conditions, an asymptotic approach to the linear solution should still occur.

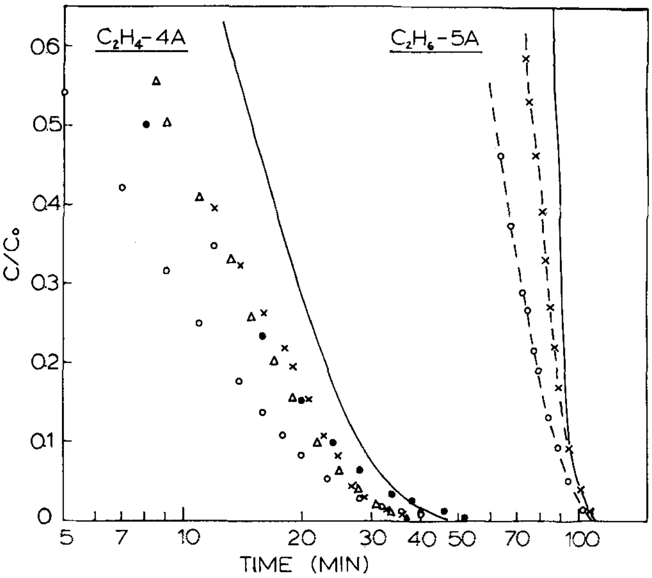

Fig. 2. Comparison of experimental desorption curves for ethylene-4A and ethane-5A with curves predicted from the linear model. (Sheth; run 7, ●; run 9, x; run 10, △, run 11, ○. Garg; run 21, x, run 27, ○.)

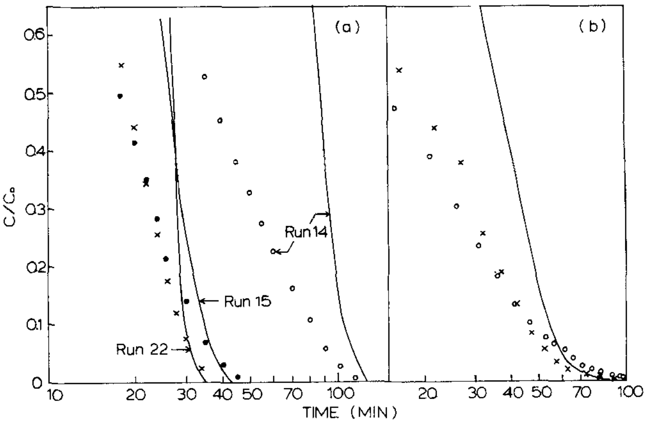

Fig. 3. Comparison of experimental desorption curves for carbon dioxide-4A with theoretical curves calculated from the linear model: (a) Runs carried out under isothermal conditions; (b) Nonisothermal data of Chandrasekaran.

TABLE 1. DETAILS OF EXPERIMENTAL CONDITIONS, HENRY'S LAW CONSTANTS AND DIFFUSIONAL TIME CONSTANTS FOR THE PREDICTION OF DESORPTION CURVES FROM THE LINEAR ROSEN MODEL

Source of data	Run	Sorbate	Sorbent	T (°K)	z (cm)	v (cm · s^{-1})	K_c	D_e/R^2 (s^{-1})	λ
Garg (1972)	21	2.16% C_2H_6-He	3.2 mm (5A)	323	91.5	5.7	350	3.6×10^{-3}	0.05
	27	8.0% C_2H_6-He							0.23
Sheth (1969)	9	1.98% C_2H_4-He	1.6 mm (4A)	323	5.3	22	4 600	5×10^{-4}	0.25
	10	2.9% C_2H_4-He							0.28
	7	4.1% C_2H_4-He							0.30
	11	5.9% C_2H_4-He							0.33
Unpublished data from this laboratory	14	0.7% CO_2-He	1.6 mm (4A)	323	15.5	30	13 700	7.4×10^{-4}	0.45
	15	0.7% CO_2-He	1.6 mm (4A)	348			3 900	2.84×10^{-3}	0.16
	22	0.7% CO_2-He	~1.0 mm (4A)	348			3 900	11.4×10^{-3}	0.16
Chandrasekharan (1962)	30.11	6.2% CO_2-Air	3.2 mm (4A)	406	102	117	400	3.7×10^{-3}	—
	31.11								

C_2H_6-5A: Micropore diffusion control. K_c is calculated from gravimetric data of Ruthven and Loughlin (1972). D_e/R^2 is taken as D_o/r_z^2, where D_o is the limiting zeolitic diffusivity at zero concentration from Ruthven, Derrah, and Loughlin (1973).

C_2H_4-5A: Micropore diffusion control. K_c and $D_e/R^2 = D_o/r_z^2$ are estimated from the nonlinear analysis of Garg and Ruthven (1974*a*), taking account of both adsorption and desorption curves.

CO_2-4A: Macropore diffusion control. K_c is calculated from data of Kiselev (1968). D_e/R^2 is taken as $\epsilon_p D_p/K_p R^2_p$, where the macropore diffusivity (D_p) is estimated in the usual manner from the molecular and Knudsen diffusivities using a tortuosity factor of 2.0 (Sargent and Whitford, 1971).

The value of $\lambda = q_o/q_s$ measures the deviation of the equilibrium isotherm from linearity.

In Figures 2 and 3 experimental desorption curves for several nonlinear systems are compared with the theoretically calculated curves from the linear Rosen model. Brief details of the experimental conditions and the parameters of the linear solution are summarized in Table 1, and further details may be found in the original papers. The limiting theoretical curves for the linear model were calculated using independently determined diffusivities and equilibrium constants and thus represent true a priori predictions.

For ethylene in 4A sieve and ethane in 5A sieve (Figure 2), the controlling resistance is micropore diffusion (Garg and Ruthven, 1974*a*), whereas for the sorption of carbon dioxide in 4A sieve (Figure 3) macropore resistance is dominant. This is shown clearly by the effect of particle size in runs 15 and 22. The effect of increasing sorbate concentration is illustrated by the data of Sheth (1969). Corresponding to the increasing nonlinearity of the equilibrium isotherm, there is an increasing deviation from the asymptotic linear solution, but the latter still provides a reasonably good prediction of the limiting desorption time.

The desorption curves of Chandrasekharan (1962) were obtained nonisothermally under conditions which approximate industrial practice. After saturation at room temperature, the bed was desorbed using a dry air stream preheated to about 165°C. Owing to heat losses, the temperature at the column outlet reached only 133°C, and the theoretical asymptotic linear curve is calculated for isothermal desorption at this temperature.

The experimental data for the systems considered here confirm the validity of using the asymptotic linear solution to predict desorption times. The full solutions to the nonlinear desorption problems which have been reported previously are of academic interest in that they show that the behavior of these systems conforms to theoretical expectations. However, from the point of view of process design, the simplified approach which is proposed here would appear to be more than adequate for most systems.

ESTIMATION OF MODEL PARAMETERS

Rosen's solution gives the dimensionless concentration as a function of a dimensionless column length parameter (3X) and a dimensionless time parameter (2*T*). For micropore diffusion control

$$X \equiv \left(\frac{D_z}{r_z^2}\right)\left(\frac{1-\epsilon}{\epsilon}\right)\cdot\frac{K_p z}{v}$$

and

$$T \equiv (D_z/r_z^2)(t - z/v)$$

For macropore control

$$X' = \left(\frac{\epsilon_p D_p}{R_p^2}\right)\left(\frac{1-\epsilon}{\epsilon}\right)\cdot\frac{z}{v}$$

$$T' \equiv \left(\frac{\epsilon_p D_p}{R_p^2}\right)\cdot\left(\frac{t - z/v}{K_p}\right)$$

For large X, the solution approximates to

$$c/c_o = \tfrac{1}{2}\,\{1 + \mathrm{erf}\,[\tfrac{1}{2}\sqrt{15X}\,(T/X - 1)]\}\,.$$

NOTATION

c/c_o = dimensionless effluent concentration
D_z = zeolitic diffusivity
D_o = limiting zeolitic diffusivity at zero sorbate concentration
D_p = macropore diffusivity
K_c = dimensionless Henry's law constant based on crystal volume
K_p = dimensionless Henry's law constant based on pellet volume $[K_p = w(1 - \epsilon_p)K_c]$
r_z = effective radius of a zeolite crystal
R_p = effective radius of molecular sieve pellet
t = time
w = fraction of zeolite crystals in solid adsorbent material
v = interstitial fluid velocity
z = column length
ϵ = voidage of packed bed
ϵ_p = macroporosity of molecular sieve pellet

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