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The Comparison of Operating Time between Batchwise and Columnwise Adsorption

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Abstract

The performance of separation processes for batchwise and columnwise adsorption with rectangular isotherms was compared. Experiments were carried out for the ion-exchange system of sodium hydroxide aqueous solution and MR-type cation exchange resin. The operating time was compared based on adsorption efficiencies with respect to the recovery of the solute and the utilization of adsorbent. Batchwise adsorption often required a shorter time than columnwise adsorption. The batchwise operation was more advantageous for greater mass transfer rate, larger adsorbent particles, and a shorter column.

INTRODUCTION

Adsorption from a solution by solid adsorbents has been widely used to recover valuable materials and to remove pollutants from solution.

The operation of an adsorption process can be classified in two different modes. The first one is a batch mode in which adsorbents are contacted with liquid in a stirred tank. The other is a column or fixed-bed mode. The columnwise operation is commonly used in industry. When

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the concentration in the liquid phase is very low, a large amount of liquid must be passed through the fixed-bed column until the breakthrough point is reached. When the flow rate is very high, the operating time can be reduced but the adsorption cannot be performed efficiently. Additionally, when the feed contains cloggy materials, filtration is required.

These problems can be solved by using batchwise adsorption. However, in regard to the elution or desorption stage, batchwise oepration may result in low efficiency in terms of both the volume of eluent and the concentration of the recovered materials.

From these consideration, a combined batchwise adsorption and columnwise elution process would be useful. Figure 1 shows a schematic of our apparatus. Solutes in solution and adsorbents are well mixed in a stirred tank. After adsorption equilibrium is reached, the valve is opened and the adsorbents are sedimented in the lower column due to gravity. The solutes in the adsorbents are desorbed to flow eluents, and the adsorbents rise to the upper stirred tank with an upflow of solution. This procedure can be repeated. The combined process has been proposed for protein separation by Goto et al. (*1*) and Brummelhuis (*2*).

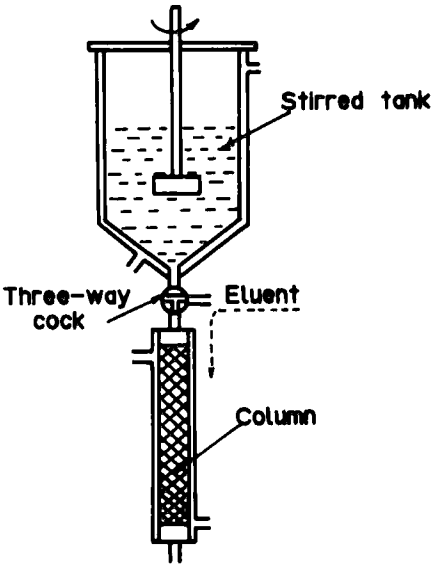

FIG. 1. Schematic of apparatus for the combined process.

The purpose of this paper is to extend the idea of a combined process to a general adsorption system. In order to evaluate the effectiveness of the combined process, the operating time and efficiency of adsorption are compared between the batch and the column modes. For the adsorption in aqueous solutions, the adsorption isotherms are frequently strongly nonlinear, such as a rectangular one.

Batchwise adsorption is promising, especially for a system of rectangular isotherms, because the solute can be completely recovered from the solution. Thus, an ion-exchange system with sodium ions in the solution and hydrogen ions in the ion-exchange resin was chosen because the adsorption isotherm was of the rectangular type (*3*).

THEORY

When an aqueous solution of NaOH contacts a strongly acidic cation-exchange resin, the ion-exchange reaction is followed by an instantaneous irreversible reaction, i.e., neutralization (*4*). The consecutive reactions can be expressed by

$$R-H^+ + NaOH \rightarrow R-Na^+ + H_2O \tag{1}$$

For this system, the adsorption isotherm is of the rectangular type:

$$q = q_m \tag{2}$$

Theoretical descriptions of batchwise and columnwise adsorption processes were developed for rectangular isotherms as follows. The adsorption rate is controlled by liquid-film mass transfer and intraparticle diffusion. Intraparticle diffusion can be represented by the shrinking-core model developed for gas-solid reactions. The rate-determining step in the particle is assumed to be pore diffusion. A theoretical analysis of both batchwise and columnwise systems is developed based on the above assumptions.

Batchwise Adsorption

The mass balance in a batchwise adsorption vessel is given by

$$qW = V(C_0 - C) \tag{3}$$

By introducing $\alpha = Wq_0/VC_0$, the above equation can be rewritten as

$$q/q_0 = (1 - C/C_0)/\alpha \tag{4}$$

where q_0 is the solid-phase concentration in equilibrium with an initial concentration in the liquid phase, C_0. The value of q_0 equals the adsorption capacity of the adsorbent, q_m, for a rectangular isotherm. The adsorption isotherm and operating lines are shown in Fig. 2. The slope of the operating line is given by $-1/\alpha$.

The adsorption efficiencies defined by the following equations are introduced as a measure of adsorption performance at equilibrium:

$$\eta_{c,\infty} = 1 - C_\infty/C_0 \tag{5}$$

(recovery efficiency of the solute in feed solution)

$$\eta_{q,\infty} = q_\infty/q_0 \tag{6}$$

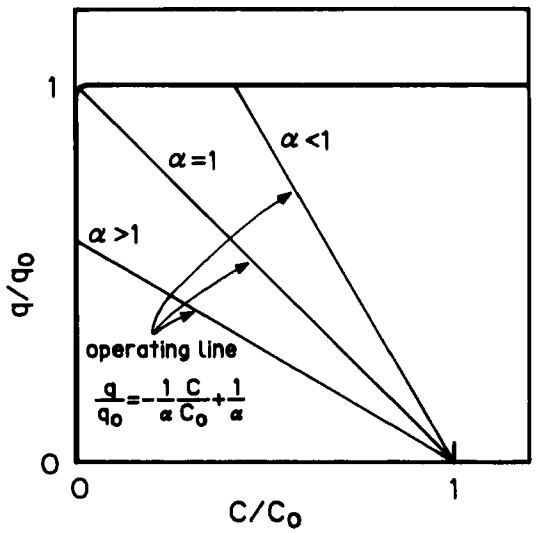

FIG. 2. Adsorption isotherm and operating lines.

(utilization efficiency of the adsorbent capacity). These efficiencies are given as follows by using Eqs. (2) and (4):

$$\eta_{c,\infty} = \alpha, \eta_{q,\infty} = 1 \qquad \text{for } \alpha < 1 \tag{7}$$

$$\eta_{c,\infty} = 1, \eta_{q,\infty} = 1/\alpha \qquad \text{for } \alpha > 1 \tag{8}$$

When α is unity, both $\eta_{c,\infty}$ and $\eta_{q,\infty}$ are unity.

Although the concentration in the solution initially decreases rapidly, the adsorption rate becomes slow as adsorption approaches equilibrium. Thus, the adsorption stage may be terminated before equilibrium is attained. The adsorption efficiencies are given as follows by using the fractional attainment to equilibrium, F ($= (C_0 - C)/(C_0 - C_\infty)$):

$$\eta_c = F\eta_{c,\infty}, \qquad \eta_q = F\eta_{q,\infty} \tag{9}$$

The kinetic equation for batchwise adsorption was derived in the case of $\alpha < 1$ by Suzuki and Kawazoe (*5*). It is also applicable for $\alpha > 1$ by introducing a parameter given by $a = (\alpha^{-1} - 1)^{1/3}$. The kinetic equation is given by

$$\tau = \frac{(1 + a^3)(1 - \mathrm{Bi}^{-1})}{3} \ln \frac{\xi^3 + a^3}{1 + a^3} + \frac{1 + a^3}{3a} \ln \frac{\xi + a}{1 + a}$$
$$- \frac{1 + a^3}{6a} \ln \frac{\xi^2 - a\xi + a^2}{1 - a + a^2} + \frac{1 + a^3}{\sqrt{3a}} \left(\tan^{-1} \frac{2 - a}{\sqrt{3a}} - \tan^{-1} \frac{2\xi - a}{\sqrt{3a}} \right) \tag{10}$$

$$\xi = [(C - C_\infty)/(C_0 - C_\infty)]^{1/3} = (1 - F)^{1/3} \tag{11}$$

where $\mathrm{Bi} = k_f R/D_e$ and $\tau = (C_0/\rho_p q_0) D_e t/R^2$.

The kinetic equation for $\alpha = 1$ is given by

$$\tau = \xi^{-1} - (\mathrm{Bi}^{-1} - 1) \ln \xi - 1 \tag{12}$$

Columnwise Adsorption

Various operating parameters are to be considered for evaluation of the columnwise performance. The breakthrough curve is shown schematically in Fig. 3. The shape of the curve is affected mainly by equilibrium and the flow rate. Not only the shape of curve but the selection of the

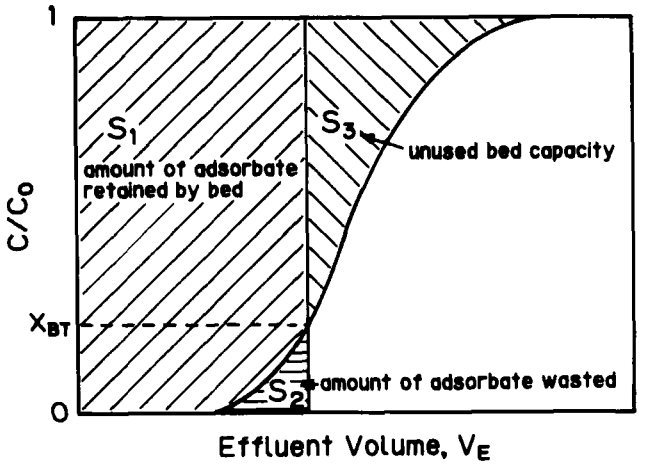

FIG. 3. Breakthrough curve for the columnwise adsorption.

breakthrough point affects the efficiencies of adsorption. The adsorption efficiency for the column is given as follows:

$$\bar{\eta}_c = S_1/(S_1 + S_2) \tag{13}$$

(recovery efficiency of the solute in feed solution)

$$\bar{\eta}_q = S_1/(S_1 + S_3) \tag{14}$$

(utilization efficiency of the adsorbent bed capacity). The values S_1, S_2, and S_3 indicate the area of the shadowed portions in Fig. 3. The breakthrough time t_{BT} corresponds to the operating time. The values of $\bar{\eta}_c$, $\bar{\eta}_q$, and t_{BT} are important to evaluate the performance of columnwise adsorption.

The spreading of the breakthrough curve is due to the finite mass transfer, the adsorption rate, and the axial dispersion. When the flow rate is low, the decrease in the spreading of the curve results in large $\bar{\eta}_c$ and $\bar{\eta}_q$. However, the operating time becomes long. When a high flow rate is used in order to reduce the operating time, the selection of the breakthrough point greatly affects the adsorption efficiency.

Kinetics in columnwise adsorption were developed by Hall et al. (*6*) under constant-pattern conditions. The theoretical model was construct-

ed on the assumption of both intraparticle and liquid film diffusion controlling and negligible axial dispersion. Breakthrough curves are calcualted by using the analytical solution.

EXPERIMENTS

Since data for batchwise adsorption were published in our previous work (*7*), only columnwise adsorption was carried out. The inside diameter of the column was 6.0×10^{-3} m and the length was 0.032 m. The column was kept at 303 K with a constant temperature jacket.

The adsorbent used was a MR-type cation-exchange resin, Amberlyst 15 in the hydrogen form. The average diameter of the swollen resin was 0.386×10^{-3} m. The solute was sodium hydroxide, and the concentration was 0.5 mol/m^3. The concentration of sodium hydroxide in the solute was continuously monitored by a conductivity meter.

EXPERIMENTAL RESULTS

The ion-exchange capacity of the adsorbent was 2.28 mol/kg-wet resin (*3*). Batchwise adsorption was performed for various kind of vessels in the previous paper (*7*). The liquid film mass transfer coefficient, k_f, was calculated from concentration changes in the solution on the assumption of liquid film mass transfer controlling. The values of k_f were in the range of $1-7 \times 10^{-4}$ m/s, depending on the agitation.

The results for columnwise adsorption are shown in Fig. 4. Broken lines indicate results calculated by the equations of Hall et al. (*6*). For the calculation, the liquid film mass transfer coefficient was estimated by Dwivedi's correlation (*8*). The diffusivity of sodium hydroxide in water was estimated to be 2.17×10^{-9} m^2/s. As a result of curve fitting, the intraparticle effective diffusivity was found to be 7.6×10^{-8} m^2/s.

DISCUSSION

The dynamic behavior of batchwise and columnwise adsorption is compared in terms of adsorption efficiencies η_c and η_q. For the comparison, the dynamics of adsorption were simulated by using the parameters obtained in the experiments. The shape of a column is

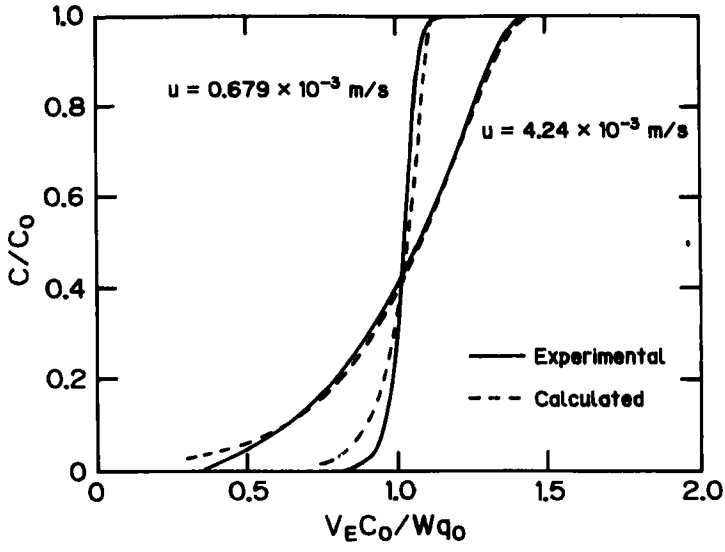

FIG. 4. Comparison between experimental and calculated breakthrough curves.

represented by geometry factor g, which is the ratio of length to diameter. Typical parameters used in the simulation are shown in Table 1.

For columnwise adsorption, the breakthrough curves for various flow rates are calculated, and the efficiencies $\bar{\eta}_c$ and $\bar{\eta}_q$ are evaluated for various breakthrough points.

Figure 5 shows the contour lines of $\bar{\eta}_c$ and $\bar{\eta}_q$ as a function of the flow rate and the breakthrough point. The operating time corresponding to Fig. 5 is shown in the same coordinates in Fig. 6.

When the operating parameter α and F are given for batchwise adsorption, the efficiencies η_c and η_q are determined from Eq. (9), and the operating time for the batch mode is calculated from Eq. (10) or Eq. (12).

To compare the operating time between batchwise and columnwise adsorption, efficiencies determined for the columnwise adsorption are designated in Fig. 5. The operating time for the operation is determined from Fig. 6. For example, when η_c and η_q were determined to be 0.8 and 0.9, respectively, for the batchwise adsorption, the corresponding point for columnwise adsorption is the point indicated by a circle in Fig. 5. The operating conditions for that point are read from the figure. The point

TABLE 1
Parameter Values Used in the Calculation

q_m = 2.28 mol/kg-wet resin
k_f = 5 × 10^{-4} m/s (stirred tank)
D_e = 7.58 × 10^{-8} m^2/s
g = 5
d_p = 0.385 × 10^{-3} m
L = 0.032 m
ε_B = 0.4

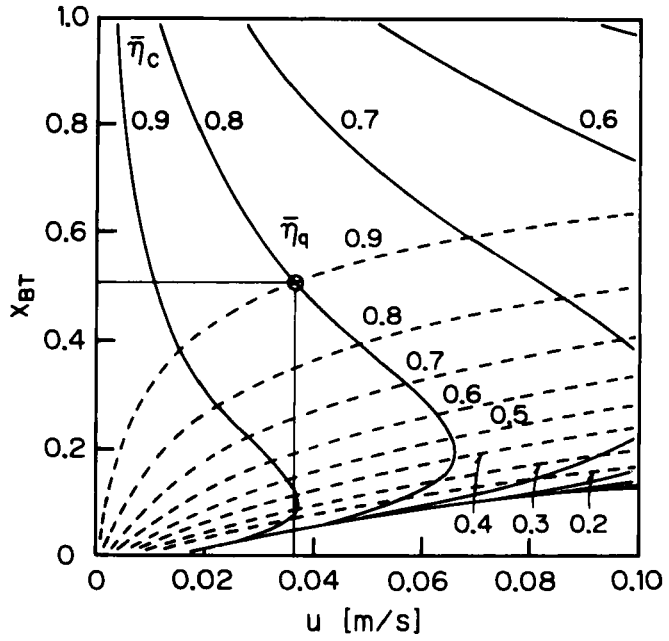

FIG. 5. Adsorption efficiencies for the columnwise adsorption.

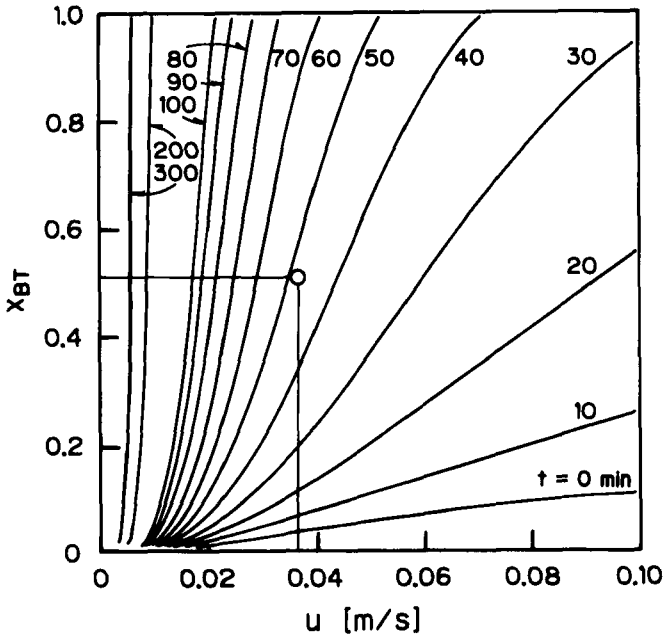

FIG. 6. Operating time for the columnwise adsorption.

corresponds to the same operating conditions is plotted in Fig. 6. The operating time for the point can be read to be 48 min from the figure. As a result, the ratio of operating time of the batch to that of the column is obtained. The same procedures from Fig. 5 to Fig. 6 are repeated to obtain the ratios for other parameters.

Figure 7 shows the ratio of the operating time as a function of α for various F. As the fractional attainment to equilibrium, F, increases, the ratio of operating time decreases, that is, batchwise adsorption becomes more effective than columnwise adsorption in terms of operating time. It is desirable for the value of F to approach unity, because the purpose of adsorption is commonly either the recovery of valuable materials or the removal of toxic materials.

Figure 8 shows the effect of the liquid film mass transfer coefficient in the stirred tank. Since the liquid film mass transfer resistance is significant in this work, the ratio of the operating time depends on mass transfer coefficients. The mass transfer resistance can be reduced for batchwise operation by vigorous agitation or by a rotating basket-type

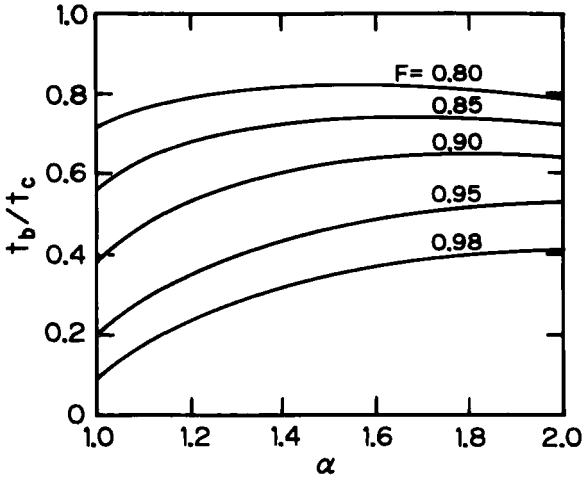

FIG. 7. Effect of fractional attainment to equilibrium.

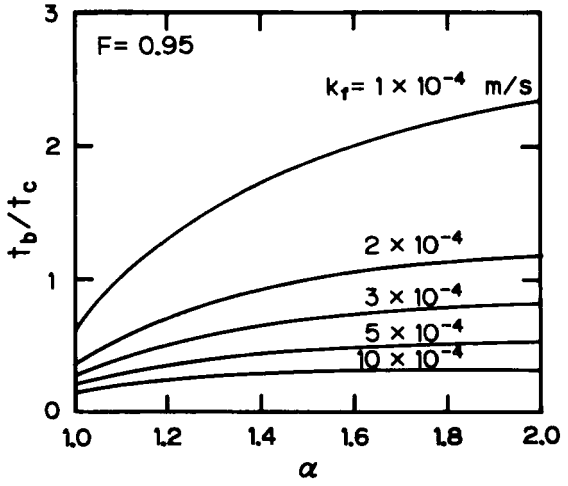

FIG. 8. Effect of liquid film mass transfer coefficient.

adsorber. On the other hand, since the mass transfer resistance depends on the flow rate and the geometry of the column for columnwise operation, it cannot be reduced easily.

Figure 9 shows the effect of adsorbent particle diameter. As the diameter increases, the operation becomes profitable to the batch mode.

Figure 10 shows the effect of the geometry of the column. The geometry factor, g, for the industrial scale is usually smaller than 10. Since the efficiency of a column decreases for small g, the columnwise operation is unprofitable.

CONCLUSION

Batchwise and columnwise adsorption were compared based on experimental results. Batchwise adsorption becomes more advantageous in terms of operating time than columnwise adsorption for a larger mass transfer rate, greater adsorbent particles, and shorter columns.

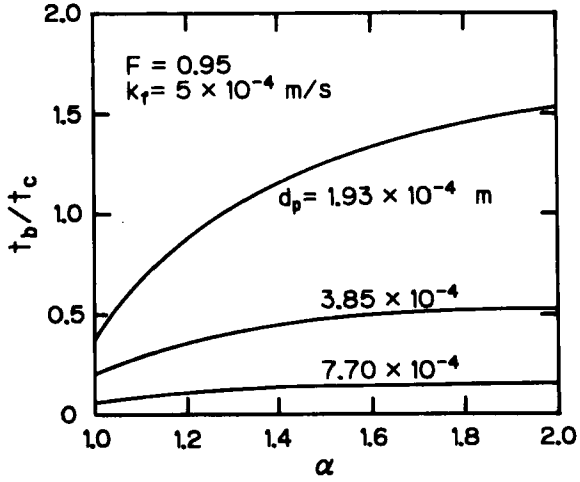

FIG. 9. Effect of particle diameter.

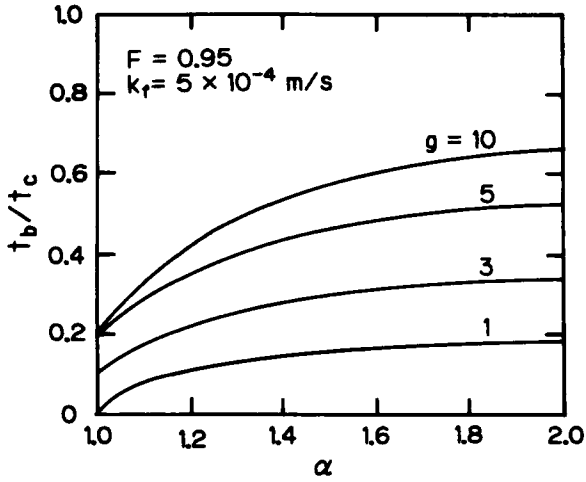

FIG. 10. Effect of geometry factor of the column.

SYMBOLS

a	$= (\alpha^{-1} - 1)^{1/3}$ (-)
Bi	Biot number (-)
C	solute concentration (mol/m^3)
C_0	feed concentration (mol/m^3)
D	diameter of column (m)
D_e	intraparticle diffusivity (m^2/s)
F	fractional attainment to equilibrium (-)
g	geometry factor of the column, L/D (-)
k_f	liquid film mass transfer coefficient (m/s)
L	bed length (m)
q	adsorbed amount (mol/kg)
q_0	solid-phase concentration in equilibrium to C_0 (mol/kg)
q_m	maximum capacity of adsorbent (mol/kg)
R	particle radius (m)
t	time (s)
t_b	operating time for batchwise adsorption (s)
t_c	operating time for columnwise adsorption (s)
u	superficial flow rate (m/s)
V	volume of liquid (m^3)

V_E effluent volume (m^3)
W mass of adsorbent (kg)
x_{BT} breakthrough point (-)

Greek Letters

α $= Wq_0/VC_0$ (-)
ε_B bed voidage (-)
η_c adsorption efficiency defined by Eq. (9) (-)
η_q adsorption efficiency defined by Eq. (9) (-)
$\bar{\eta}_c$ adsorption efficiency defined by Eq. (13) (-)
$\bar{\eta}_q$ adsorption efficiency defined by Eq. (14) (-)
ξ $= [(C - C_\infty)/(C_0 - C_\infty)]^{1/3}$ (-)
ρ_p density of adsorbent (kg/m^3)
τ dimensionless time, $(C_0/\rho_p q_0)D_e t/R^2$(-)

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