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Optimization of Lysine Adsorption Process Using Strong Cation-Exchange Resin

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Abstract

A simplified method is proposed for determining the optimum conditions of multicolumn adsorption of lysine from a lysine fermentation broth, in which the resin columns periodically move countercurrent to a continuous broth flow. Experimental data on dynamic isotherms in the fixed-bed column are required for the calculations. The recurrence equation involved was solved on a personal computer. Based on this model, the optimum operation conditions of lysine adsorption were determined in order to minimize the production cost of lysine recovery from lysine fermentation broth.

INTRODUCTION

Lysine is used in the hydrochloride form as a feedstuff for monogastric animals. It is produced by a fermentation method. For the recovery of lysine from fermentation broth, strong cation-exchange resins of the ammonium form are widely employed in commercial plants (*1*).

In the design of the adsorption column process of lysine from fermentation broth, the effluent properties were analyzed and a model for the breakthrough curve was presented (*2*). By using this model together with laboratory data on such equilibrium properties as selectivity coefficients for cationic species in the fermentation broth and the mass balance, it has been possible to predict the performance of the column adsorption process by breakthrough behavior. However, adsorption processes with higher efficiencies have been found in a multicolumn adsorption process operated under periodic countercurrent conditions, where the fluid phase flows continuously in one direction and the adsorption columns move periodically in the opposite direction (*3*, *4*). It is necessary to optimize the operating conditions for the adsorption process with different compositions of lysine fermentation broth, which vary with the carbon source and the microorganism used, in order to make the production cost of lysine more commercially profitable.

In this paper the dynamic adsorption isotherm of lysine on a strong cation-exchange resin of the ammonium form is determined from breakthrough curves at various pHs of the lysine fermentation broth. Then the optimum operation conditions were calculated to maximize the amount of lysine adsorbed onto the first column in the multicolumn adsorption process by solving the recurrence equation derived from the following mathematical model with dynamic programming and employing the aid of a personal computer NEC-9801E. We also examined whether changes in the amount of lysine adsorbed onto the first column could be validated by using the above operation conditions. Finally, we undertook to find an optimum arrangement, such as the number of resin columns in series of the fixed-bed adsorption for a given lysine fermentation broth, and the pH.

MATHEMATICAL MODEL

A mathematical model to describe the multicolumn series, which is shown in Fig. 1, can be formulated by the following equation based on the countercurrent model (5), where the stated variables are the concentration of lysine in the effluent from the jth resin column, $X_{i,j}$; the amount of lysine adsorbed onto the jth resin column, $Y_{i,j}$; the total number of resin columns, N; the volume of resin, V_r; and the volume of the broth fed to the resin column, V_b. The material balance is described by

$$V_b(X_{i,j} - X_{i,j-1}) = V_r(Y_{i,j-1} - Y_{i,j-2}) \tag{1}$$

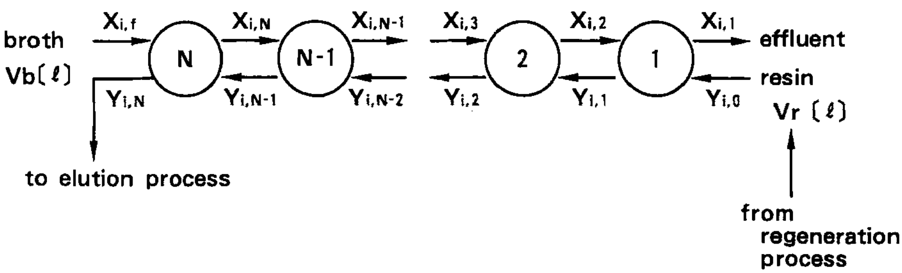

FIG. 1. Schematic diagram of multistage countercurrent adsorption process (merry-go-round system)

i	cationic species in broth; lysine
$X_{i,j}$	concentration of i-cation in effluent discharged from the jth stage (mol/L)
$Y_{i,j}$	amount of i-cation adsorbed in resin of the jth stage (mol/L)

From Eq. (1), in terms of j with the assumption that the ratio of V_b to V_r remains constant throughout all the resin columns, we obtain

$$Y_{i,j} = Y_{i,j-1}\{(X_{i,f} - X_{i,1})/(X_{i,j} - X_{i,1})\} \tag{2}$$

where the subscript f denotes the broth, so $X_{i,f}$ is the concentration of lysine in the broth fed to the resin column, and the column j was numbered backward as shown in Fig. 1. Both the optimum value of the amount of lysine adsorbed onto the resin and the concentration of lysine in the effluent from the column are obtained by solving Eq. (2) by the dynamic programming method (*6*). The objective function $F_{i,j}$ is the maximum amount of lysine on the resin column and is defined as

$$\begin{aligned} F_{i,j} &= V_b(X_{i,f} - X_{i,1}) \\ &= \text{maximum } Y_{i,j} \end{aligned} \tag{3}$$

In this algorithm the pH of the lysine broth fed to the resin column is supposed to be constant during the adsorption process. The function $F_{i,j}$ denotes the constrained maximum function of $Y_{i,j}$; then the recurrence equation of dynamic programming is expressed as follows:

$$F_{i,j} = \text{maximum } F_{i,j-1}P(X_{i,j}) \tag{4}$$

where

$$P(X_{i,j}) = (X_{i,j} - X_{i,1})/(X_{i,f} - X_{i,j})$$

Equation (4) is the relationship which constitutes the mathematical model; this permits prediction of the multicolumn adsorption process at the stationary state of operation.

Computation

A personal computer program was written in BASIC for the multicolumn adsorption process under periodic countercurrent operation. The computer prints out the calculated values for the effluent concentration of lysine and the average amount of lysine adsorbed onto the resin column for each column in the series when the value of $X_{i,1}$ is given as a predetermined constant.

EXPERIMENTAL

(1) Experimental Apparatus and Resin Used

Figure 2 shows a schematic representation of the experimental apparatus. This apparatus was used for the following experiments by changing the number of resin columns connected: 1) measurements of breakthrough curves for broth pH values of 2.0, 4.0, and 6.0, with a constant concentration of lysine fermentation broth fed to the resin column; and 2) measurement to confirm the amount of lysine adsorbed onto each column under the given conditions which had been calculated on an NEC-9801E computer for three columns in series during the adsorption process (Table 1).

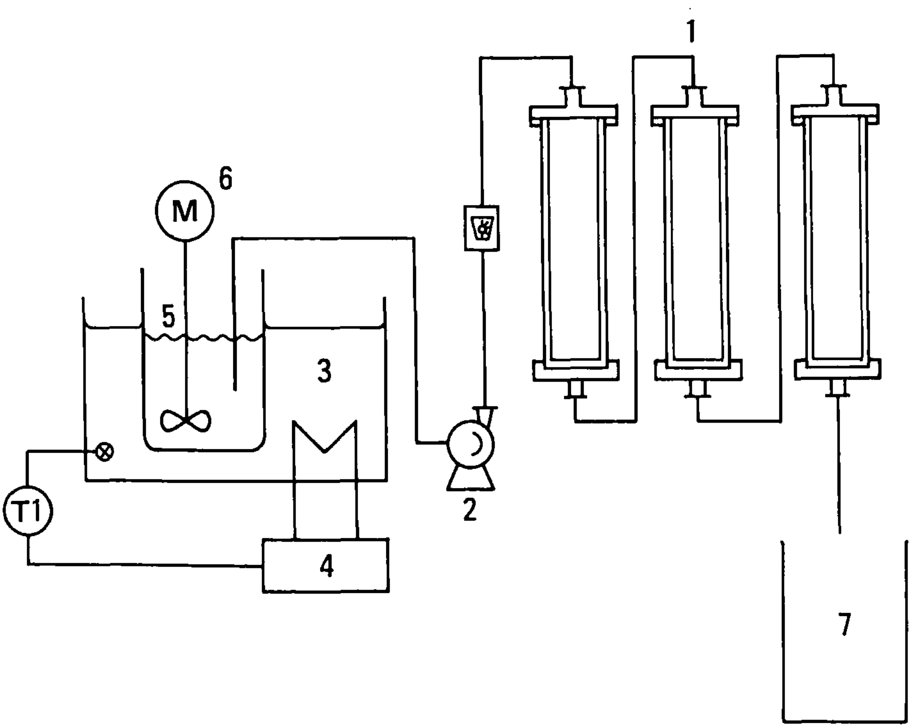

FIG. 2. Experimental apparatus.

1: resin columns made from glass (50 mm × 250 mm)
2: peristaltic pump
3: water bath with thermometer
4: thermoregulator
5: 5-L glass beaker for feed solution
6: agitator with motor
7: 10-L beaker made from polystyrene for effluent

TABLE 1
Typical Experimental Conditions and Results for a Three-Column Adsorption Process. (fixed value: flow rate of broth = 2.0 L/h; $X_{i,1}$ = 0.0055 mol/L)

	Lysine broth			Simulation results,	Experimental results			
Run	pH	$X_{i,f}$	V_b/V_r	$Y_{i,3}$	$Y_{i,3}$	$Y_{i,2}$	$Y_{i,1}$	$X_{i,1}$
1	2	0.323	1.54	0.493	0.488	0.209	0.052	0.0082
2	4	0.372	1.67	0.625	0.646	0.264	0.073	0.0038
3	6	0.361	1.58	0.572	0.584	0.130	0.026	0.0055

The lysine fermentation broth was cultivated with hydrolyzed starch as the main carbon source with various microorganisms. The composition was as follows (mol/L): lysine (as hydrochloride salt) 0.434, ammonium ion (as nitrogen) 0.15, total nitrogen 1.51, potassium ion 0.023, sodium ion 0.330, sulfate ion 0.03, and chloride ion 0.123.

The resin columns were made of glass cylinders of 50 mm i.d. and 250 mm length (1), and the flow rate of the broth was precisely regulated by a peristaltic pump (2). The strong cation-exchange resin employed was DIAION-SK IB (Mitsubishi Kasei Kogyo Co., Ltd.) of the ammonium form with 8% DVB (divinylbenzene), an average particle diameter of 0.68 mm, a water content of 47.6%, and an ion-exchange capacity of 1.93 meq/mL.

Procedures

(1) Measurement of Breakthrough Curves

One liter of carefully weighed ammonium form resin was packed into the column and backwashed for about 30 min with distilled water to remove air from the column. The column was placed in a vertical position, and the water was maintained at a constant level during the experiment. The pH of the broth was adjusted with 35% hydrochloric acid, and the broth was fed at a predetermined flow rate by a peristaltic pump at 2.0 L/h from the top of the resin column until the effluent from the bottom of the column showed the same pH as that of the influent. During this experiment, while maintaining the water level, 10 mL effluent was withdrawn by a syringe at 15 min intervals and the pH was measured with a pH meter (Toa Denpa Kogyo Co., Ltd, Model 40-S), and lysine was determined with an amino acid analyzer (Hitachi Co., Ltd, Model 835). The breakthrough curves obtained at pH 2.0, 4.0 and 6.0 were individually integrated graphically to determine the amount of lysine adsorbed, Y_i, as a function of the concentration of lysine in the effluent, X_i. These adsorption isotherms, obtained experimentally, were utilized to calculate the recurrence equation (Eq. 4).

(2) Validation of the Calculated Results for Three Columns in Series

Six resin columns which contained 1.0 L of the ammonium cation-exchange resin were provided for the adsorption experiment with three columns in series. The overall scheme of the resin process during the steady-state of the six-column operation is illustrated by Fig. 3. Each resin column was operated in a cycle as follows. Column B, which was used as the second column in the former cycle, was used as the first column. Column F, which was regenerated with dilute acidic water to adjust the pH to neutral, was

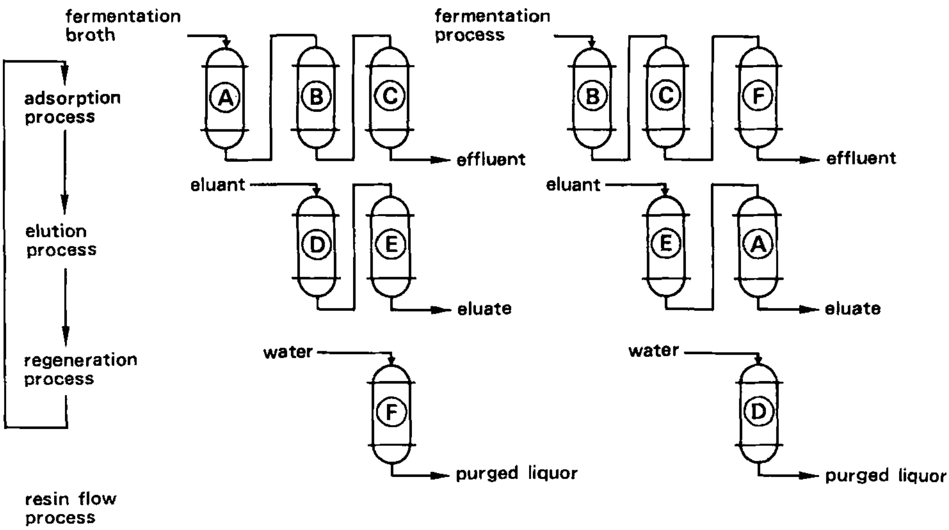

FIG. 3. Schematic diagram of resin process.

then connected to the trail, and Column C was moved to the second position. These three columns, B, C, and F in series, were used for the adsorption process, and Column A, which was the first column in the former cycle, became the trail column of the two-columns in series for the elution process with 2-*N* ammonia water as the eluant. After passing a calculated volume of broth through the columns, 1.5 times the bed volume of distilled water was applied to transfer the remaining portion of broth in each resin column into the next column.

After five cycles, the three columns connected in series for the adsorption process were detached, and then each column was eluted with 2 times the bed volume of 2-*N* hydrochloric acid solution, followed by 1.5 times the bed volume of distilled water. The eluate was then analyzed for lysine.

RESULTS AND DISCUSSION

(1) *Dynamic Adsorption Isotherms for Fixed-Bed Column*

Figure 4 shows the breakthrough curves for the three different pH values of the lysine broth. The saturated amount of lysine adsorbed, $Y_{i,f}$, in equilibrium with $X_{i,f}$ obtained by graphical integration, was as follows (in mol/L): 0.618 at pH 2.0, 0.796 at pH 4.0, and 0.758 at pH 6.0. It is evident

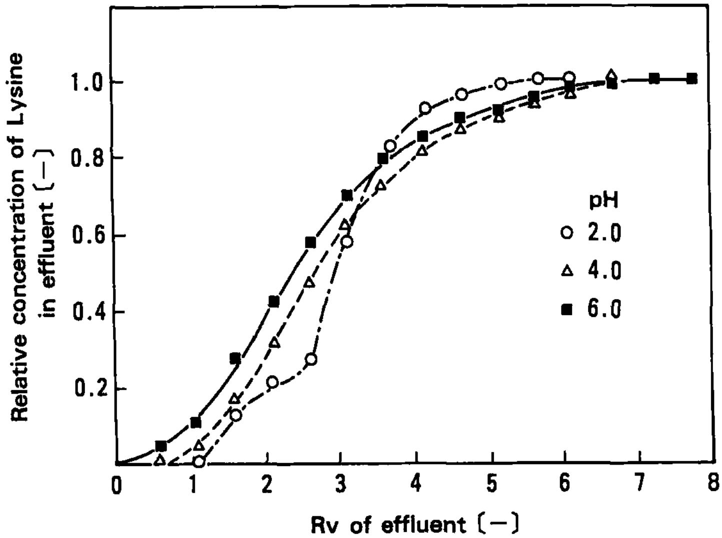

FIG. 4. Breakthrough curve of lysine.

from these results that the amount adsorbed at pH 4.0 shows the maximum amount of lysine adsorbed value for the lysine fermentation broth used.

Dynamic adsorption isotherms between the amount of adsorbed lysine, Y_i, and the concentration of lysine in the effluent, X_i, for the respective pHs of the broth fed to the resin column were obtained by graphical integration of the breakthrough curve. The dynamic adsorption curves were within the permissible range of error, using the following three-order polynomial functional equations,

$$Y_i = 0.171 + 4.07X_i - 7.62X_i^2 + 0.608X_i^3, \quad \text{for pH 2.0}$$

$$Y_i = 0.156 + 3.01X_i - 4.01X_i^2 + 2.62X_i^3, \quad \text{for pH 4.0} \qquad (5)$$

$$Y_i = 0.054 + 7.10X_i - 30.8X_i^2 + 55.4X_i^3, \quad \text{for pH 6.0}$$

The regression coefficients for the above equations were 0.991 at pH 2.0, 0.99 at pH 4.0, and 0.996 at pH 6.0.

(2) Validation of the Simulation Results

The countercurrent model for the multicolumn adsorption process was computed for the adsorption of lysine, $X_{i,j}$, on the resin column, $Y_{i,j}$, with changes in the number of resin columns in series. In Fig. 5 the calculated

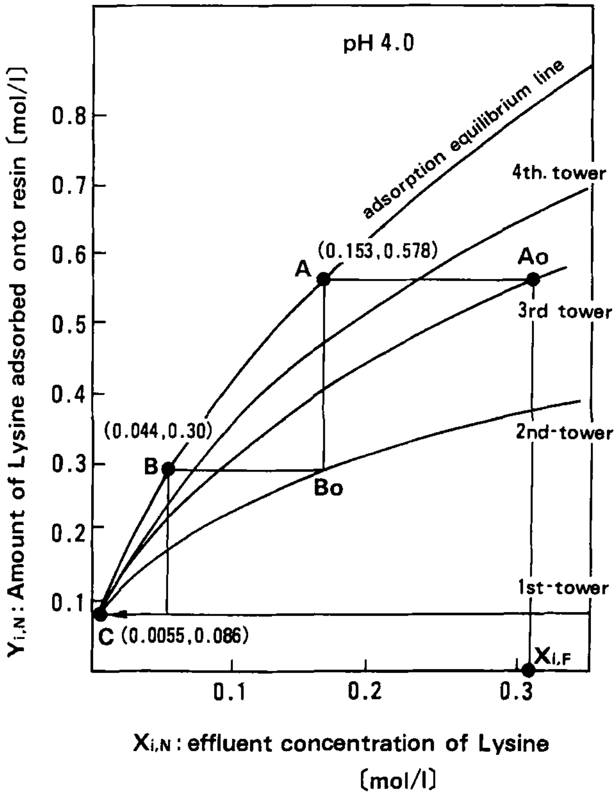

FIG. 5. Simulation results for the determination of optimal adsorption strategy with a multistage column.

curves for the amounts of lysine adsorbed at pH 4.0 are plotted against the lysine concentration in the effluent as a function of the number of columns in series, where the value of $X_{i,1}$ was fixed at 5.5×10^{-3} mol/L. From this figure the optimum volume of broth (V_b) fed to the resin column with various numbers of columns in series for the pH value of the broth is given by

$$V_b = V_r(Y_{i,N} - Y_{i,N-1})/(X_{i,f} - X_{i,N}) \quad (6)$$

where $Y_{i,N}$ is the amount adsorbed onto the first column with N resin columns connected in series.

Validation of the optimum condition calculated from Eq. (6) was performed on a three-column adsorption process with changes in the lysine concentrations of the broth. Comparisons of calculated conditions and the experimental results obtained after five cycles of the respective conditions are shown in Fig. 6, where solid lines represent the dynamic isotherm for the respective pHs of the broth fed to the column. As can be seen, the calculated values of both the first and second columns for the respective broth pHs agree well with the experimental values, but for the final column a slight deviation from the isotherm's curve is observed for each pH of the broth. This can be attributed to the effect of backmixing, which was neglected in the simulation, and the degree of deviation would be negligible in commercial production. As shown in the simulation results, determination of the operation conditions for a given broth can be readily performed.

(3) Optimum Operation of the Adsorption Process

Optimum conditions to minimize production cost were explored based on the method presented. Consideration focused on the optimum operation conditions for the amount of lysine produced: 1000 t/month (as hydrochloride salt). The conditions employed for the calculation are listed in Table 2.

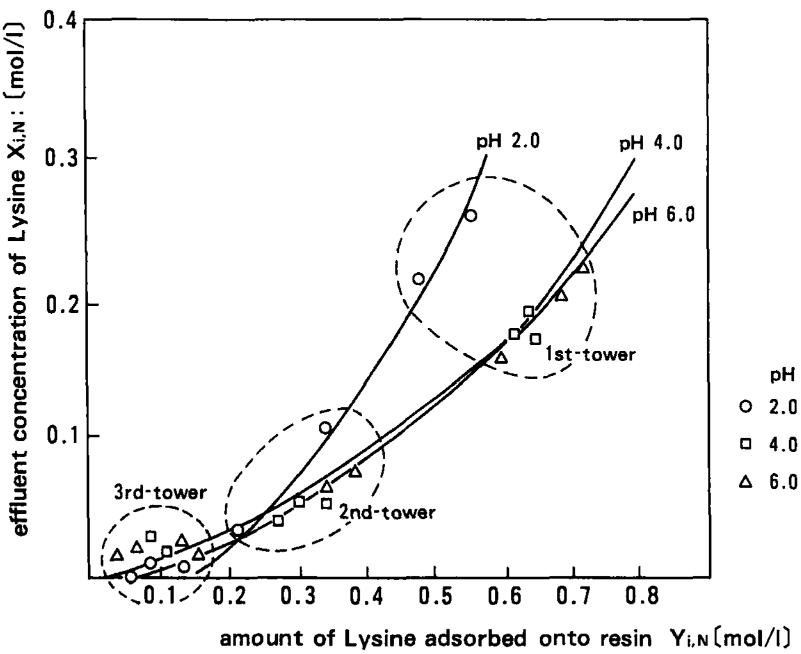

FIG. 6. Comparison of experimental and calculated values for the relationship between $Y_{L,N}$ and $X_{L,N}$.

TABLE 2
Conditions Used to Estimate the Optimal Cost for the Lysine Adsorption Process

1) Resin operation
   a) Number of cycles per day = 10
   b) Resin volume required to pack a resin column = $1000/(10)(28)Y_{i,N}$, where 10 is the number of cycles per day and 28 is the number of operation days per month available
   c) $X_{i,1}$ = 0.0055 mol/L
2) Concentration of lysine in fermentation broth, $X_{i,f}$ = 0.306

The variables examined were: 1) the number of resin columns, and 2) the pH value of the lysine fermentation broth. These values are summarized in relation to the amount of lysine adsorbed onto the first resin column; $Y_{i,N}$ in arbitrary numbers of resin columns in series, as shown in Fig. 7, which represents the relationship between $Y_{i,j}$ and the number of columns, N, for four different pH conditions. As expected, the amount of lysine adsorbed onto the resin increased with an increase in the number of columns, but a slight change in the amount of lysine adsorbed was observed with more than four columns in series for each broth pH.

The production cost is composed of variable cost and fixed cost. Variable

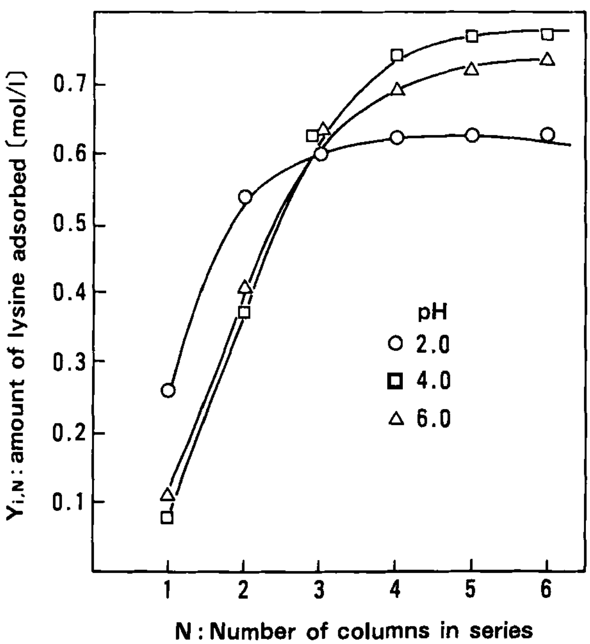

FIG. 7. Relationship between $Y_{L,N}$ and N.

cost, which includes the sum of the costs of 35% hydrochloric acid, 28% ammonia water, and the resin consumed in the resin process, is

$$V = aV_1 + bV_2 + cV_3 \tag{7}$$

where a, b, and c are unit costs for the respective materials, and V_1, V_2, and V_3, which are the amounts of 35% hydrochloric acid, 28% ammonia water, and resin consumed, are expressed by

$$V_1 = Y_{i,N}V_3S(36.5)/(0.35), \qquad \text{for 35\% hydrochloric acid}$$

$$V_2 = Y_{i,N}V_3G/L, \qquad \text{for 28\% ammonia water}$$

where G and L are given by;

$$G = K_{\mathrm{NH_4^+}}^{\mathrm{Lys^+}}/(1 + (\mathrm{H^+})/k_1) + 2K_{\mathrm{NH_4^+}}^{\mathrm{Lys2^+}}/(1 + k_1/(\mathrm{H^+}))$$

$$L = K_{\mathrm{NH_4^+}}^{\mathrm{Lys^+}}/(1 + (\mathrm{H^+})/k_1) + K_{\mathrm{NH_4^+}}^{\mathrm{Lys2^+}}/(1 + k_1/(\mathrm{H^+}))$$

and

$$V_3 = (1000)(10^3)/(30)(10)(182.65)Y_{i,N}K, \qquad \text{for resin}$$

In these relations, $K_{\mathrm{NH_4^+}}^{\mathrm{Lys^+}}$ and $K_{\mathrm{NH_4^+}}^{\mathrm{Lys2^+}}$ are the selectivity coefficients of mono- and dilysine cations for the ammonium ion as reported elsewhere (*7*), $(\mathrm{H^+})$ is equivalent to $10^{-\mathrm{pH}}$, k_1 is the first dissociation constant of lysine, K is the number of cycles of resin used periodically, which was determined based on economical optimization as reported previously (*8*), and S is the molar ratio of hydrochloride to lysine required for the adjustment of pH in lysine fermentation broth, and obtained experimentally with

$$\log S = -0.164\mathrm{pH} + 0.71$$

The fixed cost (F) includes depreciation for the construction cost of the resin tower:

$$F = A(N + 3)V_3^{0.6}/7 \tag{8}$$

where A is the unit construction cost of a resin tower ($\$/\mathrm{m}^3$) and N is the amount of resin required for the adsorption process. The number 3 in Eq. (8) is the additional number of resin towers required for the elution and regeneration process to operate a number of resin processes in parallel.

The constant value 7 is the depreciation ratio determined by the straight-line method for 7 years.

The production cost, J, is therefore set up as

$$J = V + F$$

$$= B + (C/Y_{i,N}) + D[E(N + 3)/Y_{i,N}]^{0.6} \quad (9)$$

where B and C are constants related to the material unit cost which is summarized from Eq. (7), and D and E are constants for fixed costs evaluated from Eq. (8).

The second term of Eq. (9) is inversely proportional to the value of $Y_{i,N}$. The third term is inversely proportional to $Y_{i,N}^{0.6}$. Figure 8 shows the relationship between the relative production cost and the number of columns with variable broth pH. It is seen that the production cost sharply decreases at first with an increasing number of columns, the minimum cost is attained with four columns in series, and it then again increases with an increase in the column number irrespective of the pH of the broth fed to the resin column. The minimum cost conditions were also determined to be four columns in series with a pH of 4.0 for lysine recovery from the fermentation broth cultivated with hydrolyzed starch in this experiment. The theoretical

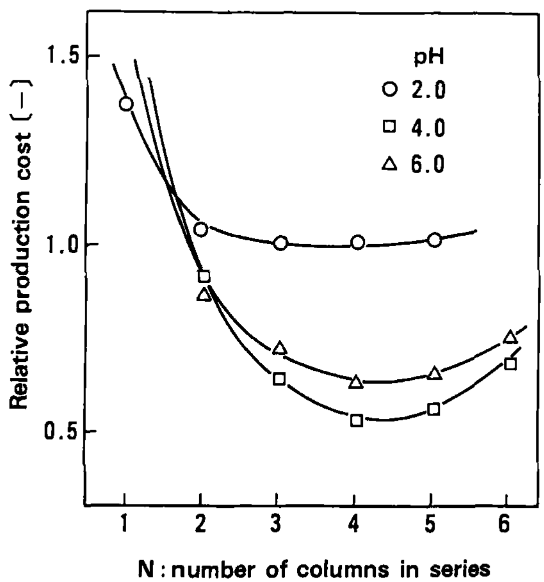

FIG. 8. Relationship between relative production cost and N.

treatment proposed here for the optimum operation of an adsorption process could also be applied to other adsorption processes employing multicolumn operations.

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NOMENCLATURE

a	unit cost of 35% hydrochloric acid ($/kg)
A	unit construction cost of resin tower ($/kg)
b	unit cost of 28% ammonia water ($/kg)
c	unit cost of resin ($/kg)
$F_{i,j}$	the objective function defined by Eq. (3)
(H^+)	concentration of hydrogen ion in lysine fermentation broth (mol/L)
k_1	the first dissociation constant of lysine (—)
K	the number of cyclic operations of resin used (—)
$K_{NH_4^+}^{Lys^{n+}}$	selectivity coefficient of n-cation of lysine for ammonium ion
N	number of resin towers in series
$P(X_{i,j})$	the recurrence equation defined by Eq. (4)
S	the mole ratio of hydrochloric acid to lysine for the pH in lysine fermentation broth (—)
X_i	the concentration of lysine (referred to as i-cation) in the effluent of the resin column used in the dynamic adsorption isotherm (mol/L)
Y_i	the amount of lysine adsorbed onto the resin in the dynamic adsorption isotherm expressed as a function of X_i (mol/L)
$X_{i,j}$	the concentration of i-cation in the effluent from the jth resin column (mol/L)
$Y_{i,j}$	the amount of i-cation adsorbed onto the jth resin (mol/L)
$Y_{i,N}$	the amount of i-cation adsorbed onto the first resin column with N-resin columns in series (mol/L)
V_1	the amount of 35% hydrochloric acid required to adjust the pH of lysine fermentation broth (kg)
V_2	the amount of 28% ammonia water required for the elution process (kg)
V_3	the amount of resin required to compensate for the exhausted volume per cycle (kg)
V_b	the volume of broth fed to the resin column (L)
V_r	the volume of resin packed in the column (L)

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