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Lactic Acid Fermentation and Adsorption on PVP

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ABSTRACT

Lactic acid was produced by immobilized *Lactobacillus delbreückii* cells in a fixed-bed reactor and then separated by a column packed with poly(4-vinylpyridine) as an adsorbent. Satisfactory simulation results were obtained by describing the fermentation process using a fermentation kinetics model with axial dispersion and the column adsorption process using a linear-driving-force model.

Index Entries: Lactic acid; immobilized cells; fermentation; fixed bed; PVP adsorption.

INTRODUCTION

As an organic acid widespread in nature, lactic acid can be produced either by the synthetic method or by the fermentation method. In industrial lactic acid production via the microbial route, the fermentation is carried out in the presence of an excess of calcium carbonate as a neutralizing agent in order to prevent lowering of the pH of the fermentation broth. The recovery of lactic acid is thus difficult and costly owing to the presence of salt. Since the synthetic method for the production of lactic acid is very competitive at about the same cost as the microbial method, there have been many efforts to improve the performance of the fermentation method. Poly(4-vinylpyridine) resin (PVP) was found to have a reasonable capacity for the adsorption of lactic acid without adsorption of many inorganic salts *(1)* and can be regenerated efficiently by methanol as the eluant *(2)*. A simultaneous fermentation and separation process of lactic acid in a fluidized-bed bioreactor filled with immobilized cells and PVP particles was studied *(3)*. In addition, an extractive fermentation process combining lactic acid production two-step pH manipulation and extraction of lactic acid by PVP was also developed *(4)*.

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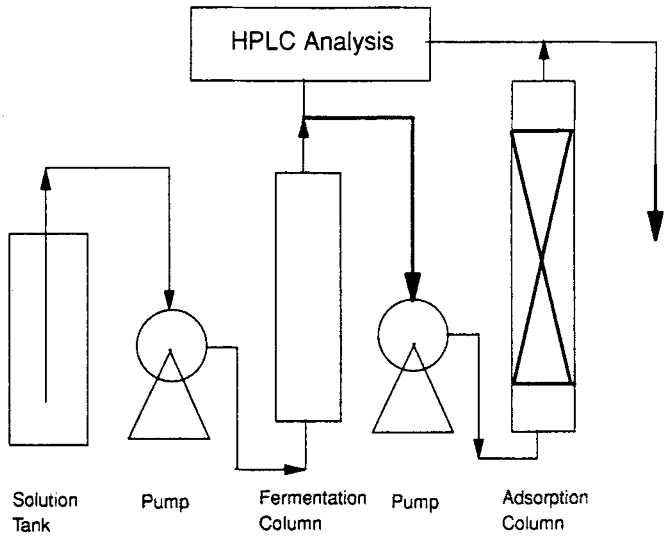

Fig. 1. Schematic of lactic acid fermentation and adsorption system.

In this article, the kinetics of lactic acid fermentation by immobilized *Lactobacillus delbreückii* cells in a fixed-bed reactor was investigated, and a generalized mathematical model was developed to account for its steady-state fermentation process. The adsorption process that separates lactic acid from the fermentation broth by a column packed with PVP as an adsorbent was studied.

MATERIALS AND METHODS

L. delbreückii was grown in media containing glucose, 5 g/L yeast extract, 0.5 g/L $(NH_4)_2SO_4$, 0.3 g/L $MgSO_4$, 0.2 g/L KH_2PO_4, and 0.2 g/L K_2HPO_4, which was sterilized by autoclaving. The initial pH was pH 5.8. Inocula were grown in the flasks at 40°C for 2 d on 10 g/L glucose and centrifuged to concentrate the cells. According to the immobilized method *(5)*, small uniform gel beads were made of 1% alginate and stabilized in a 0.1*M* $CaCl_2$ solution. The concentrated cells were added to the gel solution before forming the beads.

The fermentation experiments were performed in a packed-bed reactor filled with the immobilized *L. delbreückii* cells. The reactor has a 2.8-cm id and is 40 cm in length. The adsorption experiments of lactic acid were also performed in a packed-bed column filled with Reillex-402 PVP. The adsorption column has a 2.2-cm id and is 41 cm in length, and the bed void is around 0.3. They are shown in Fig. 1.

A Bio-Rad (Hercules, CA) HPX-87H Ion-Exclusion column was used to determine glucose and lactic acid concentration. The mobile phase was 0.005*M* H_2SO_4 at a flow rate of 0.8 mL/min at 60°C. The detector was refraction index.

MATHEMATICAL MODELS

Fermentation Process in Steady State

The mass balance for a packed-bed column can result in the following Eq.:

$$(\partial s/\partial t) = D_z\,(\partial^2 s/\partial z^2) + D_r\,(1/r)\cdot(\partial/\partial r)\,[r\,(\partial s/\partial r)] - u\,(\partial s/\partial z) - R_s \qquad (1)$$

where s = substrate (glucose) concentration (g/L), t = time (s), D_z = axial dispersion coefficient (m^2/s), D_r = radial dispersion coefficient (m^2/s), u = flow rate (cm/s), *z* = axial distance (cm), *r* = radial distance (cm), and R_s = reaction rate (g/L·s). If the process is in steady state and the radial dispersion can be negligible, Eq. 1 can be simplified as:

$$D_z\,(d^2s/dz^2) - u\,(ds/dz) - R_s = 0 \tag{2}$$

The reaction rate of the lactic acid fermentation with immobilized-cell R_s can be described by following Eq. (3). Since this is a continuous fermentation with immobilized cells in a fixed bed, cells leaked from the immobilized-cell gel beads will be brought out of the column by the fluid. Also, an assumpution can be made that the immobilized-cell beads would not be broken in the fermentation process. Thus, the bacterial number [*x*] in Eq. (3) will be a constant, which results in a first-order fermentation reaction with immobilized cells occurring in the fixed bed.

$$R_s = k \cdot s \cdot [x] \tag{3}$$

where *k* = reaction constant. Thus,

$$D_z\,(d^2s/dz^2) - u\,(ds/dz) - K \cdot s = 0 \tag{4}$$

where K = k·[*x*]. The boundary conditions are:

$$z = 0,\ s = s_0 \tag{5}$$

$$z = L,\ (ds/dz) = 0 \tag{6}$$

At the reactor exit, *z* = L, the solution for the above equations can be obtained:

$$(s/s_0) = \exp\,[(Pe/2)]\ /\ \{[\cosh(B) + (Pe/2 \cdot B)\sinh(B)]\} \tag{7}$$

where

$$B = [(Pe/2)^2 + Bi]^{1/2} \tag{8}$$

Pe and Bi are the axial Peclet number and Biot number, respectively.

$$Pe = uL/D_z;\ Bi = KL^2/D_z \tag{9}$$

For the product in the column,

$$(p - p_0)/(s_0 - s) = y_{p/s} \tag{10}$$

where $y_{p/s}$ = the yield, which is dimensionless, and p = product concentration (g/L).

Adsorption of Lactic Acid on PVP

$$u\,(\partial c/\partial z) + (\partial c/\partial t) + (1 - \varepsilon/\varepsilon)\,\rho_s\,(\partial q/\partial t) = 0 \tag{11}$$

where c = lactic acid concentration (g/L), ε = bed void (dimensionless), ρ_s = adsorbent density (g/L), and q = amount of lactic acid sorbed by the adsorbent (g/g dry PVP). The linear-driving-force model can be used for the mass-transfer process:

$$(\partial q/\partial t) = k_a\,(q^* - q) \tag{12}$$

where k_a = mass transfer coefficient (1/s), and q^* = equilibrium adsorption amount corresponding to the liquid-phase concentration c, which can be determined by the experimental isotherm.

$$q^* = H \cdot c \tag{13}$$

where H = Henry constant (g/L). The initial and boundary conditions are as follows,

$$c = 0, q = 0 \qquad \text{at } t = 0, z = z \tag{14}$$

$$c = c_0 \qquad \text{at } t = t, z = 0 \tag{15}$$

The analytical solution *(6)* for the above equations is:

$$c/c_0 = \exp(-\xi + \tau)\cdot I_0[2(\xi\tau)^{1/2}] + \exp(-\xi)\int_0^t \exp(-\chi)\cdot I_0[2(\xi\chi)^{1/2}] \cdot dx \tag{16}$$

where I_0 is the zero-order Bessel function.

$$\xi = (1 - \varepsilon/\varepsilon) \cdot (H \cdot k_a \cdot z/u); \tau = k_a \cdot [t - (z/u)] \tag{17}$$

RESULTS AND DISCUSSION

Lactic acid was produced by immobilized *L. delbreückii* cells in a fixed-bed reactor. The effect of different glucose concentrations and different flow rates during the fermentation process at the column exit is shown in Fig. 2. Satisfactory simulation results were obtained by describing the fermentation process using a mathematical model with axial dispersion. This could mean that the axial dispersion should be considered in the process model because of the smaller flow rate in the lactic acid fermentation with immobilized cells. The model parameters shown in Table 1 can be obtained by correlating from the experimental data. From Fig. 2, with the increase of the flow rate, substrate glucose concentration is increased, but product lactic acid concentration is decreased. The relationship between $\Delta s \cdot u$ ($\Delta s = s_0 - s$) and the dilution rate D (D = u/V, where V is the column void volume) is shown in Fig. 3. When the flow rate u or D is in the range of small values, increasing u will be helpful to the increase in the productivity of lactic acid, but there will be no large effect if u or D is in the range of large values.

Based on the flow rate and the diameter of the immobilized cell of about 3 mm, the Reynolds number in the column fermentor can be estimated. It is <10, which means that the laminar flow exists in the column fermentor. Therefore, the axial dispersion in the column is mainly caused by the Taylor diffusion. This argument may be supported by evidence that the axial dispersion coefficient (listed in Table 1) correlated from the experiments is much greater than the diffusion coefficient of glucose in the water.

Adsorption isotherm of lactic acid from the fermentation reactor on PVP is shown in Fig. 4. The isotherm is linear in the lower concentration of lactic acid, which is conformable with the published results *(3)*. Figure 5 shows the breakthrough curves of lactic acid in the PVP column, which are simulated satisfactorily by the linear-driving-force model, Eq. (14).

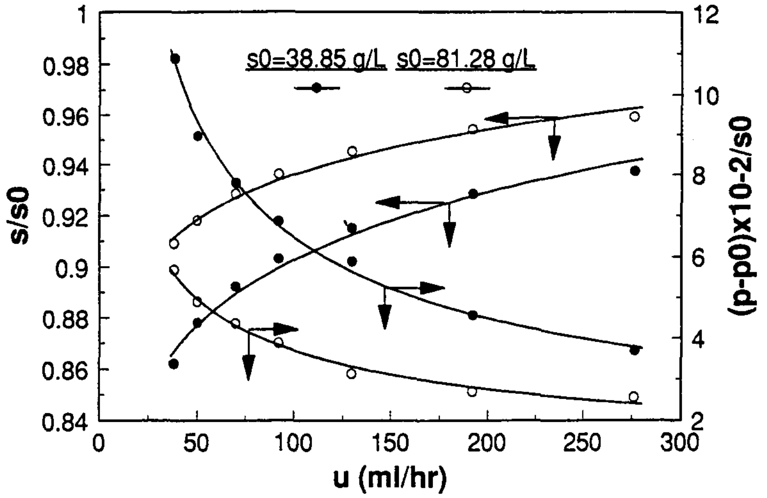

Fig. 2. Comparison between experimental glucose and lactic acid concentration and calculated concentration using the proposed model (solid curves are the calculated curves based on Eq. [7]).

Table 1
The Parameters Correlated from the Experimental Data

s_0, g/L	D_z, m^2/s	K, 1/s	$y_{p/s}$
38.85	12.651×10^{-6}	29.464×10^{-6}	0.6078
81.28	94.738×10^{-7}	29.790×10^{-6}	0.6010

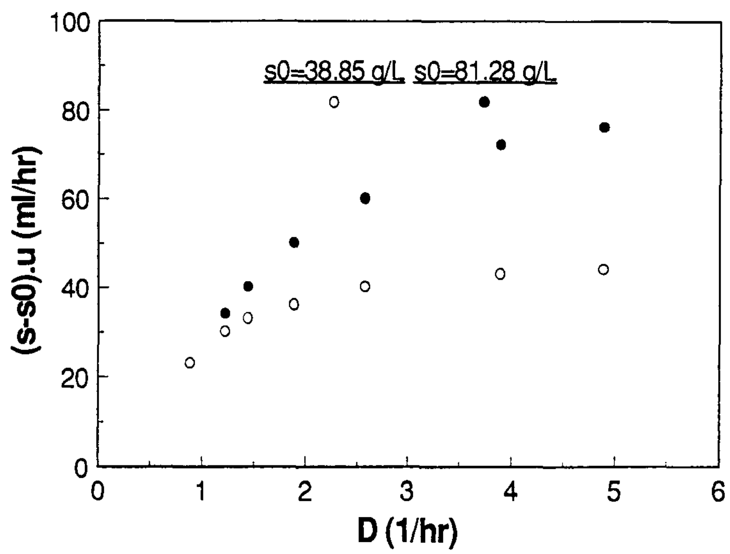

Fig. 3. The relationship between $\Delta s \cdot u$ and the dilution rate D.

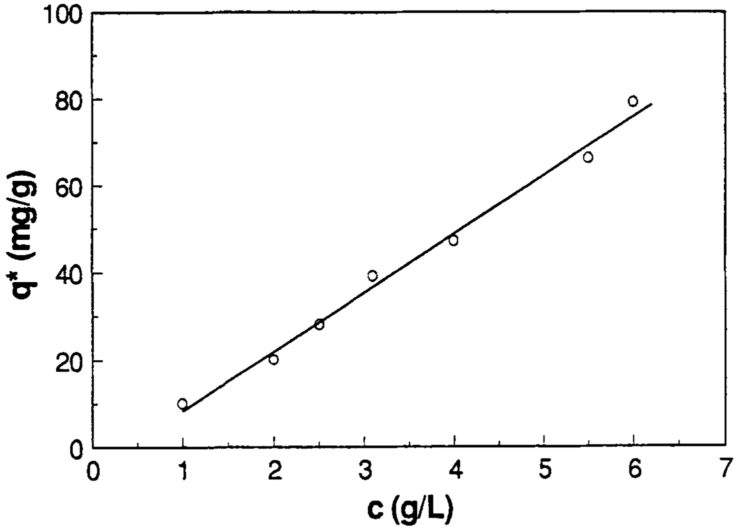

Fig. 4. Adsorption isotherm of lactic acid on PVP.

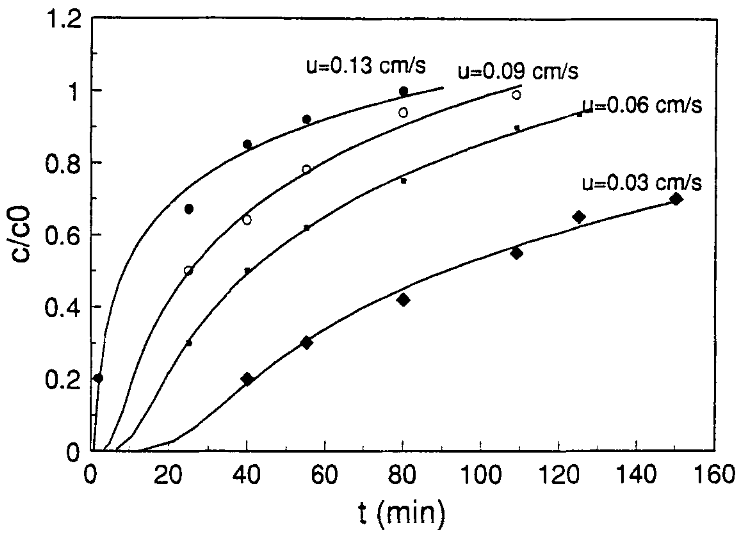

Fig. 5. Adsorption breakthrough curves of lactic acid on the PVP column (solid curves are the calculated curves based on Eq. [17]).

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