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Diffusivity of Xylitol in Granular Activated Charcoal

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ABSTRACT

The xylitol adsorption on granular activated charcoal was investigated. From the experimental observations, a non-linear adsorption isotherm of Langmuir type equation was used to describe intraparticle diffusivity of xylitol on granular activated charcoal in liquid-phase adsorption. Two Langmuir coefficients, Q_{max} = 0.2191 kg/kg and K = 0.1216 m^3/kg were estimated using linear regression analysis. Surface diffusion coefficients (D_s) were determined from adsorption rates in a finite bath using diffusion model. As a result, D_s increased with an increase of initial xylitol concentration (C_{L0}) or so called an equilibrium amount of xylitol adsorbed on activated charcoal (q_∞). This relation resulted in the following equation, $D_s = 0.7911 \times 10^{-8} \exp(5.849 q_\infty)$. In addition, for a packed bed column, a perfect mixing model gave a good fitting with experimental result under the conditions of this investigation. The simulation with perfect mixing model were demonstrated with changes of flow rates and bed lenghts. Different saturation time and no breakthrough times were figurely revealed.

Key word : xylitol, activated charcoal, diffusivity, adsorption, langmuir isotherm

INTRODUCTION

A bioreactor which encloses and circulates the biocatalysts inside a membrane module has been recently developed (Endo *et al.*, 1990). At the same time various research works with application of high density cultivation of microorganism have also been thoroughly studied (Endo *et al.*, 1990; Nakano *et al.*, 1993). A removal of inhibitiory product as well as an enhancement of productivity of the process using low growth rate organism are considered to be realized by applicable high dense culture using membrane separation system. Therefore a microbial process of xylitol production by yeast (Sirisansaneeyakul *et al.*, 1992) has to be possibly improved with an application of high density fermentation coupled with xylitol removal using activated charcoal system (Figure 1).

The studies on the production of xylitol by the above mentioned process have been divided into two aspects: (i) high density culture with hollow fiber module and (ii) separation of xylitol by using activated charcoal column. This study was thus focused on the diffusivity of xylitol in selected granular activated charcoal. The diffusion characteristics of xylitol on activated charcoal were investigated both in a finite bath adsorption and with packed bed column. The results may be applicable for design of fixed-bed column used in the proposed bioprocess of xylitol production.

MATERIAL AND METHODS

Chemicals Xylitol (248-00545) as well as

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granular activated charcoal (034-02125) were purchased from Wako Pure Chemical Industries, Ltd. The other chemicals used were also obtained from the same source as mentioned above.

Analysis Xylitol was measured colorimetrically with spectrophotometer at 412 nm by using an improved colorimetric assay for polyols (Bok & Demain, 1977).

Methods The xylitol uptake (q) was calculated from the initial concentration (C_{L0}) and the final concentration (C_{LE}) of the xylitol in solution was obtained according to the following equation :

$$q = \frac{V_L(C_{LO} - C_{LE})}{W_S} \quad (1)$$

Where V_L is the liquid sample volume and W_S is the starting sorbent weight. Adsorption isotherms were constructed from the experimental points using the Langmuir type model (Langmuir, 1916 , 1918 , Sanada *et al.*, 1992 , Suzuki, 1990).

$$q = \frac{Q_{max}KC_L}{1 + KC_L} \quad (2)$$

The experimental equilibrium coefficient (K) and the maximum uptake (Q_{max}) were determined by the following equation, to which Eq. (2) was tranformed (Yoshida *et al.*, 1994).

$$C_L = -\frac{1}{K} + Q_{max}(\frac{C_L}{q}) \quad (3)$$

The surface diffusion coefficient (D_S) of xylitol on the granular activated charcoal was obtained from a batch treatment of adsorption rate in the well stirred solution suspending the sorbents. The basic equation of surface diffusion controlling can be represented in the following dimensionlesss forms (Hashimoto *et al.*, 1975).

$$\frac{\partial Z}{\partial \theta} = \frac{\partial^2 Z}{\partial \chi^2} + \frac{2}{\chi}\frac{\partial Z}{\partial \chi} \quad (4)$$

where $Z = \frac{q}{q_0}$, $\chi = \frac{r}{R}$, $\theta = (\frac{Ds}{R^2})t$

The equilibrium curves for the Langmuir isotherms can also be represented by the following equations :

$$Z = \frac{y}{K' + (1 - K')y} \quad (5)$$

where $y = \frac{C_{LE}}{C_{L0}}$ and K' is called the separation factor which is defined as

$$K' = \frac{1}{1 + k'C_{L0}} \quad (6)$$

Then Eq. (4) - (6) can be solved numerically, when $\frac{C_{LE}}{C_{L0}}$, the ratio of the equilibrium concentration to the initial concentration and K' are given.

On the other hand, the model describing the adsorption of xylitol from a flowing liquid stream onto a fixed bed of activated charcoal, the mass transfer effects includes in the model are intraparticle diffusion, surface film diffusion and axial dispersion (Liapis and Rippin, 1978). The equation of conservation is then given by Rosen (1952).

$$u(\frac{\partial C}{\partial z}) + \varepsilon(\frac{\partial C}{\partial t}) - D_L(\frac{\partial^2 C}{\partial z^2}) = \gamma(\frac{\partial q}{\partial t}) \quad (7)$$

Where u is the constant linear flow velocity, z is the distance measured from the input face of bed, ε is the void fraction in the bed, D_L is the longitudinal or axial dispersion coefficient and γ is the density of packed bed.

At low Renolds number, a longitudinal diffusion term, $-D_L(\frac{\partial^2 C}{\partial z^2})$ on the left-hand side of Eq. (7) can not be neglected. In general, the rates of adsorption, $\gamma(\frac{\partial q}{\partial t})$ on the right-hand side of Eq. (7) can be simply expressed as follows (Nayve, 1993) :

$$\gamma(\frac{\partial q}{\partial t}) = K_F - av(C - C^*) \quad (8)$$

Where K_F is the overall mass transfer coefficient, av is the specific surface area of activated charcoal and C* is the equilibrium concentration of xylitol.

In addition, the basic equation of a perfect mixing model is generally given as follows (Sanada *et al*, 1992) :

$$\frac{dC}{dt} = \frac{F}{V_L(C_{L0} - C_L)} - D_S S \rho_P \left(\frac{dq}{dt}\right) \quad (9)$$

Where F is the flow rate, S is the surface area of particle and ρ_p is the density of the particle.

For the solution of the above described equations, the transformed dimensionless forms were solved for finite difference approximation. The value of $\frac{C_L}{C_{L0}}$ or $\frac{C_L}{C_{LE}}$ (Eq. 4-6) and the break-through curves (Eq. 7-9) were calculated on a personal computer (NEC PC-9801 RA) using Crank-Nicolson and Successive Over Relaxation (SOR) with the basic program for the approximation (Nayve, 1993).

RESULTS

1. Determination of Langmuir Adsorption Coefficients

Various sets of experiments were carried out in test tubes (25 x 200 mm) containing xylitol (1, 10, 25, 50, 100, 150 and 200 g/l) in 10 ml of phosphate buffer solution (0.05 M, pH 5.0) and granular activated charcoal (10, 25, 50, 100, 125, 150, 175 and 200 g/l). The mixtures were incubated at 30°C on the the shaker for 24 h. The supernatants after centrifugation were analyzed for final xylitol concentrations.

The adsorption isotherm by plotting the final xylitol concentrations (C_L) and xylitol uptakes (q), using Eq. (1) is shown in Figure 2B. The adsorption of xylitol on granular activated charcoal follows Langmuir type equation (Eq. 2), of which two constants, maximum uptake (Q_{max} = 0.2191 kg/kg) and equilibrium coefficient (K = 0.1216 m^3/kg) are obtained by linear regression of Eq. (3), showing the straight line without scattering (Figure 2A).

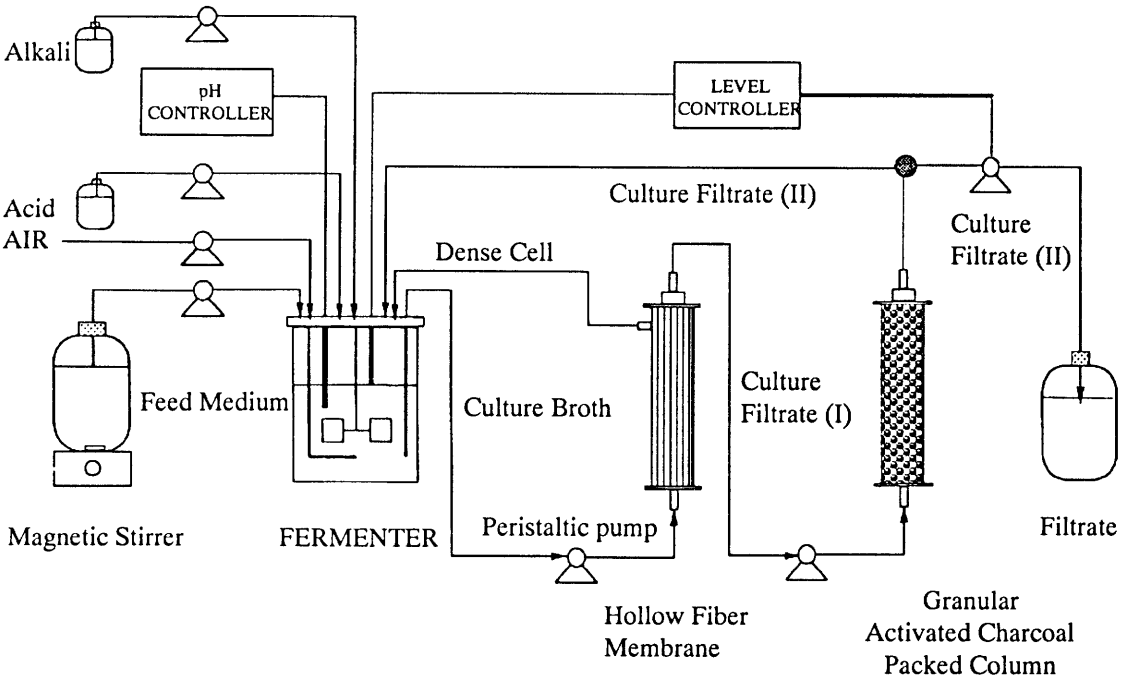


Figure 1 Schematic diagram of high cell density culture with xylitol recovery using activated charcoal.

2. Measurement of Surface Diffusion Coefficients of Xylitol into Granular Activated Charcoal

Three sets of experiments were carried out in a 1-L stirred tank (MB type, Iwashiya K. Sawada Co., Ltd.) containing 100 g/l granular activated charcoal in 500 ml of phosphate buffer solution (0.05 M, pH 5.0) with the initial xylitol concentrations of 10, 50 and 100 g/l. The incubation was controlled at 30°C and 200 rpm of agitation speed

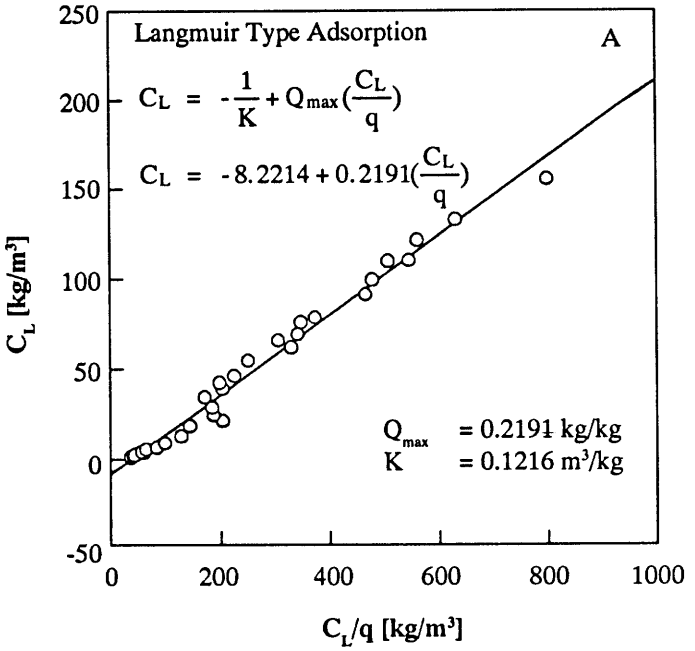


Figure 2A Determination of Langmuir coefficients by linear regression.

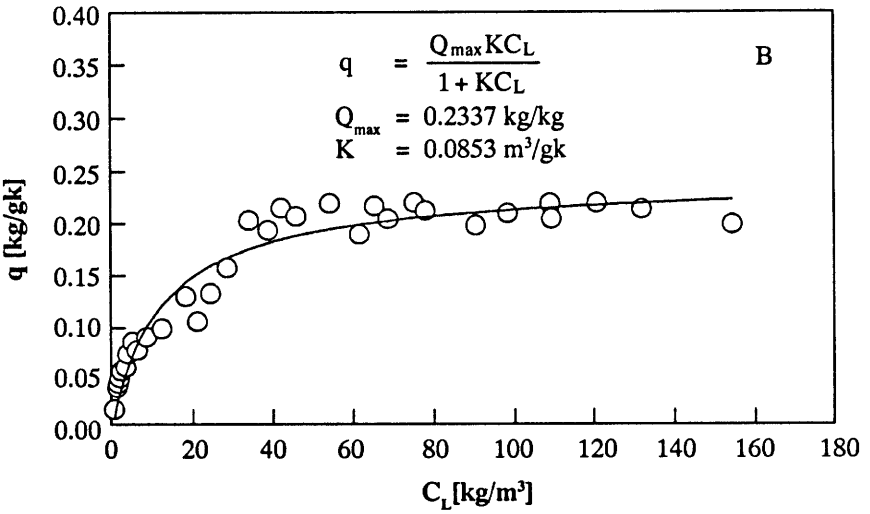


Figure 2B Langmuir adsorption isotherm of xylitol with granular activated charcoal.

for 24 h. The samples (1-2 ml) were taken at 15, 30 or 60 min intervals until 10 h. The final concentration of xylitol at 24 h was decided for equilibrium adsorption on activated charcoal and calculated for the final equilibrium amount adsorbed (q_∞).

The adsorption curves for initial xylitol concentrations of 13, 64 and 110 g/l are shown in Figure 3A, 3B and 3C, respectively. By curve fitting method, the surface diffusion coefficients were optimized following Langmuir isotherm adsorption and the values of 1.25×10^{-8}, 3.75×10^{-8} and 4.25×10^{-8} m²/min were obtained for C_{L0} = 13,

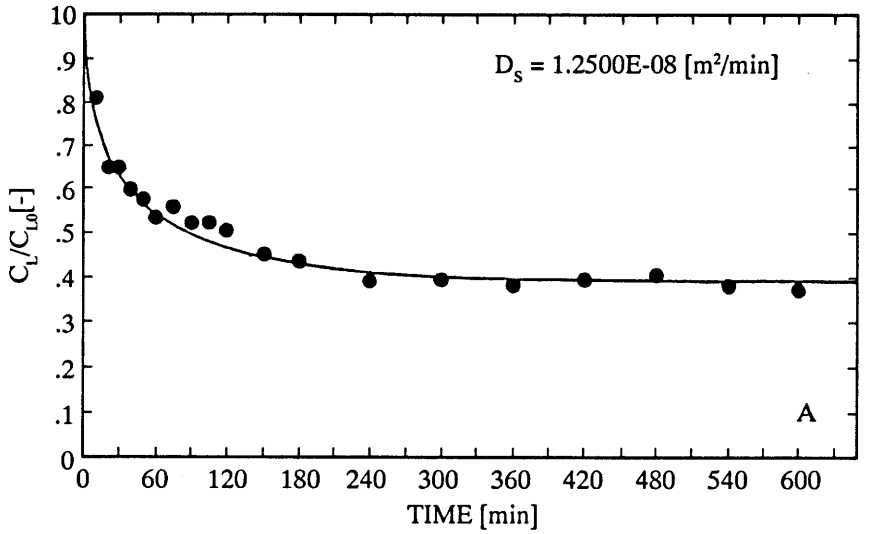


Figure 3A Adsorption of xylitol on granular activated charcoal in the stirred tank (batch treatment; C_{L0} = 13.3 g/l).

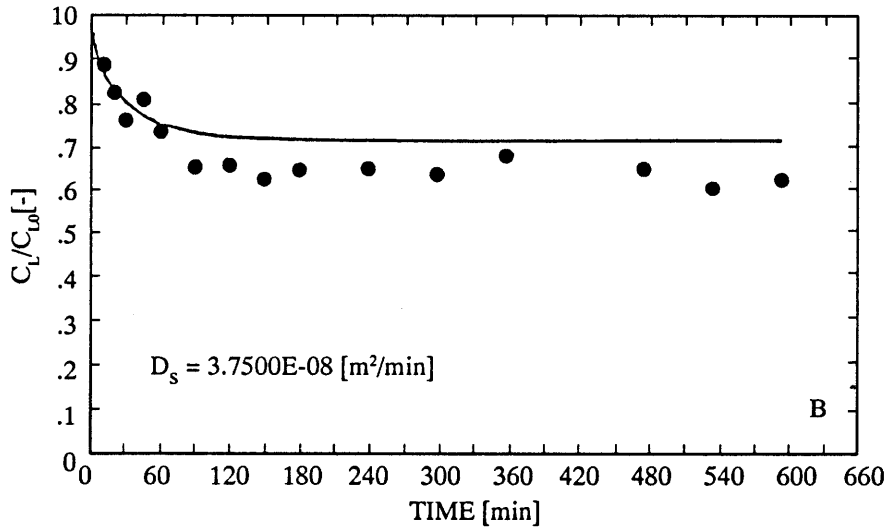


Figure 3B Adsorption of xylitol on granular activated charcoal in the stirred tank (batch treatment; C_{L0} = 64.4 g/l).

64 and 110 g/l, respectively.

The increase of D_s with q can be explained by a decrease in adsorption energy (E) with an increase in q (Itaya *et al.*, 1987, Sudo *et al.*, 1987). The values of D_s thus obtained (Table 1) were correlated as a function of the final equilibrium amount adsorbed, q_∞ as in the following equation :

$$D_S = D_S^0 \exp(kq_\infty) \quad (10)$$

Figure 4 shows the relation between D_s and q_∞ derived for Langmuir isotherm system. The $D_S^0 = 0.7911 \times 10^{-8}$ m²/min and k = 5.849 kg/kg were finally obtained.

3. Adsorption of Xylitol on Packed Bed Column of Granular Activated Charcoal

A column with 26 cm height and 5.3 cm of inner diameter was packed with 1-h boiled granular activated charcoal (273.2 g dry weight), giving the void volumn of 198 ml. The set-up of equipment for determination of breakthrough curve was shown

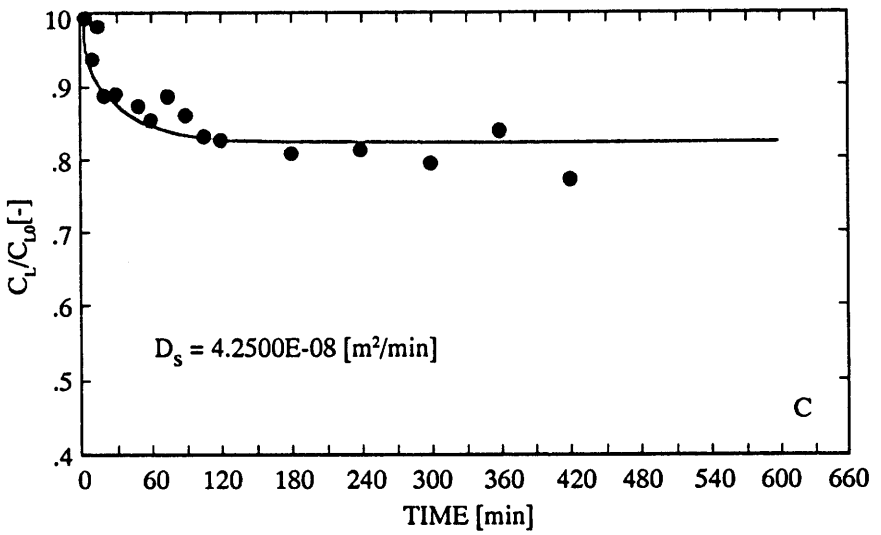


Figure 3C Adsorption of xylitol on granular activated charcoal in the stirred tank (batch treatment; CL0 = 110.1 g/l).

Table 1 Adsorption of xylitol on granular activated charcoal suspending in phosphate buffer (0.05 M, pH 5.0) in a stirred tank.

C_{L0} (g/l)	C_{LE} (g/l)	q_∞ (g/g)	D_S[(1)] (x 10^{-8} m²/min)
13.3	4.3	0.09	1.25
64.4	38.7	0.26	3.75
110.1	72.1	0.29	4.25

(1) Bycurve fitting method

in Figure 5. A feed of xylitol (C_{L0} = 20 g/l) in phosphate buffer (0.05 M, pH 5.0) with a constant flow rate (F) of 9.7 ml/min was introduced continuously into the packed column for 8 h at room temperature (27-28°C). The samplings of outlet concentration were carried out at 30 min intervals and analyzed for xylitol concentration (C_L).

The measured values of C_L against C_{L0} were

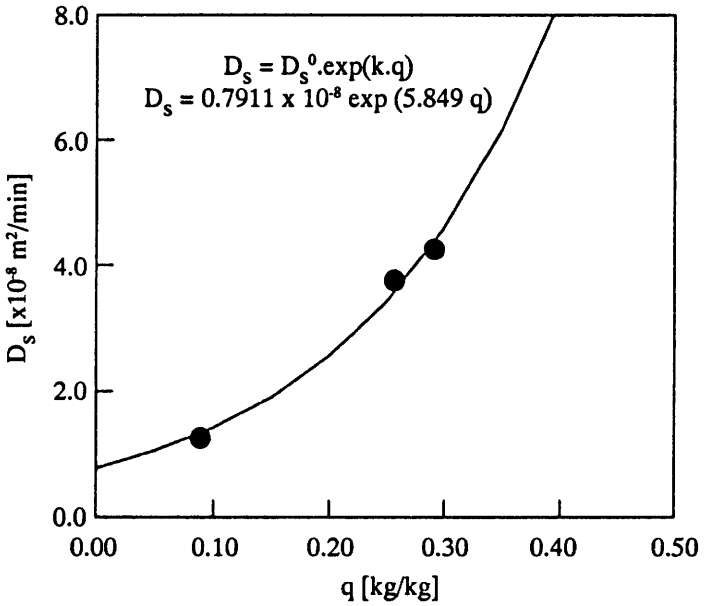


Figure 4 Relation between D_S and q derived for Langmuir isotherm system.

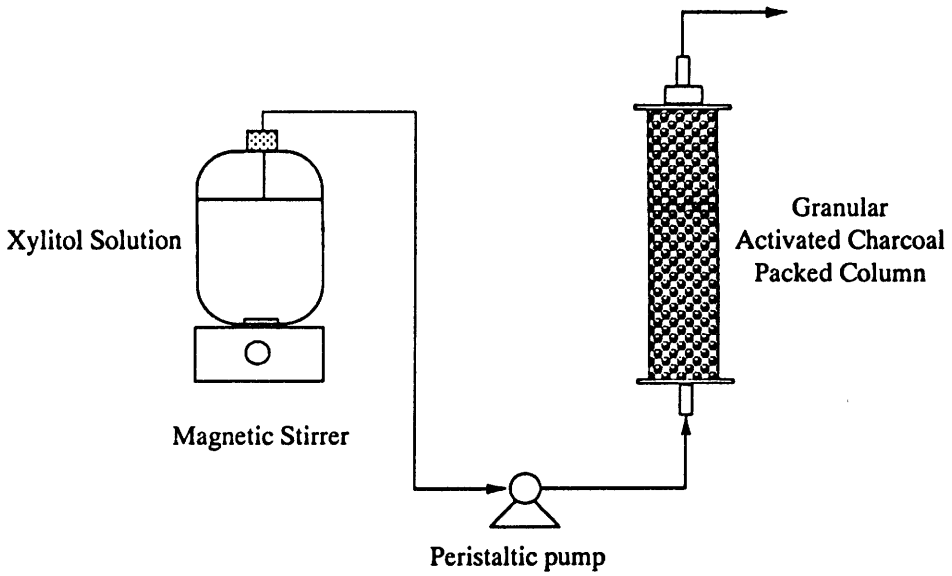


Figure 5 Schematic diagram of the equipment for determination of breakthrough curve.

plotted due to time course shown in Figure 6. At 5 h of feeding, 85 % of initial xylitol concentration was reached and a slow increase of concentration was gradually continued to 90 % at 8 h. For simulation, two models of diffusion and perfect mixing with Langmuir type isotherm were tested for fitting the experimental data. It was found that a perfect mixing model could fit fairly well to the experimental observation (Figure 6B), while a diffusion model could not (Figure 6A). It can be concluded that adsorption of xylitol on granular activated charcoal column showed a phenomenon of perfect mixing situation under the conditions set.

Furthermore, the breakthrough curves were simulated using above obtained parameters with changes of flow rates (F = 1.0-10.0 ml/min) (Figure

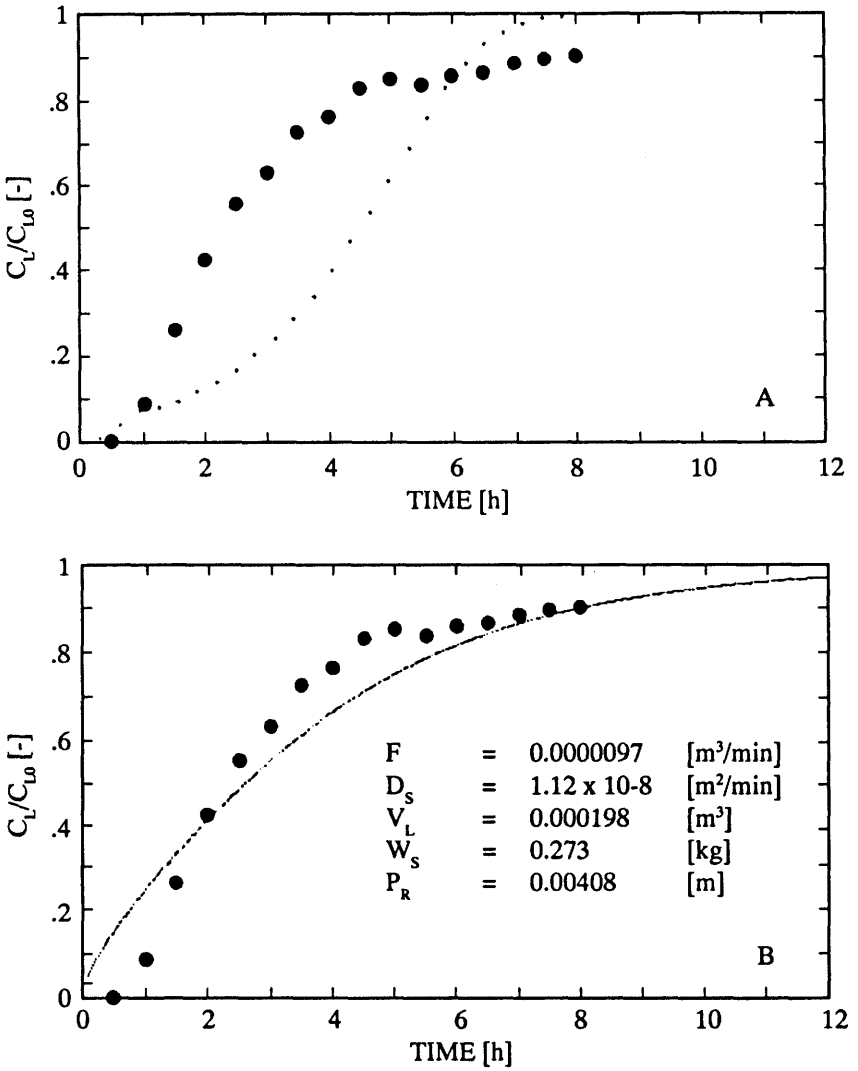


Figure 6 The breakthrough curves of xylitol with packed bed column of granular charcoal (H = 26 cm, D = 5.3 cm and F = 9.7 ml/min).
(A) Curve fitting with diffusion model (B) Curve fitting with perfect mixing model

7A) and bed lenghts (z = 25-150 cm) (Figure 7B). An increase of flow rates shortens saturation time (t_s) of the packed bed column, while an increase of bed lenghts prolongs saturation time (t_s). Using a perfect mixing model, the breakthrough time (t_b) is theoretically accounted at time zero.

4. Desorption of Xylitol from Packed Bed Column of Granular Activated Charcoal with Ethanol

A packed bed column of granular activated charcoal was saturated with xylitol (C_{L0} = 20 g/l) in phosphate buffer (0.05 M, pH 5.0) by circulating

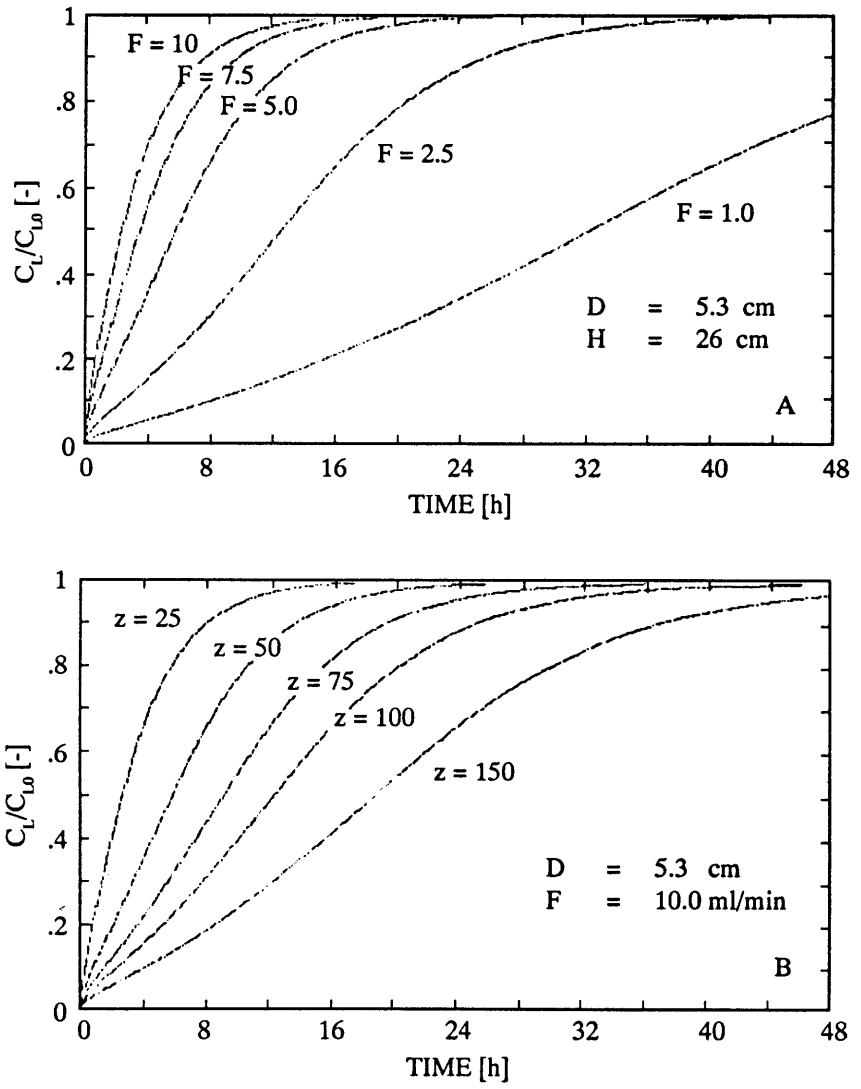


Figure 7 Simulation of the breakthrough curves with perfect mixing model (C_{L0} = 23.0 g/l, D_S = 1.12 x 10^{-8} m^2/min).

(A) Change of flow rates (F), from left-hand side : 10, 7.5, 5.0, 2.5 and 1.0 ml/min

(B) Change of bed length (z), from left-hand side : 25, 50, 75, 100 and 150 cm

such aqueous solution (5 l) for 2 days. An equilibrium concentration of xylitol was measured as C_{LE} = 14.7 g/l. Then the circulation by xylitol solution was taken off and a constant flow of ethanol (F = 10.0 ml/min) was introduced upwardly into the packed column previously saturated with xylitol (C_{L0} = 20 g/l) at room temperature (27-28°C). The samples were taken at 30 min intervals until 8 h.

The rates of xylitol desorption from packed bed column was shown in Figure 8. Within 1 h of ethanol feeding, the outlet concentration of xylitol was increased to 29.4 g/l and then decreased gradually. After 5 h of ethanol elution, the 85 % reduction of C_{LE} = 14.7 g/l was obtained and only a small further reduction of the outlet concentration was occurred until 8 h (92 %).

DISCUSSION

The adsorption of xylitol on granular activated charcoal was investigated with phosphate buffer systems using various concentrations of xylitol and amounts of activated charcoal. The Langmuir adsorption equation could provide for the explanation of a nonlinear isotherm at fairly high xylitol solution (C_{L0} = 1-200 g/l) with Q_{max} = 0.2191 kg/kg and K = 0.1216 m^3/kg. Consequently intraparticle diffusivities in liquid-phase adsorption in stirred tank were carried out for the determination of surface diffusion coefficients (D_S). The Diffusion model was introduced for optimization of D_S with three sets of experimental observations (C_{L0} = 10, 50 and 100 g/l). As a result, the surface diffusion coefficients increased with an increase of initial xylitol concentrations. It has been suggested

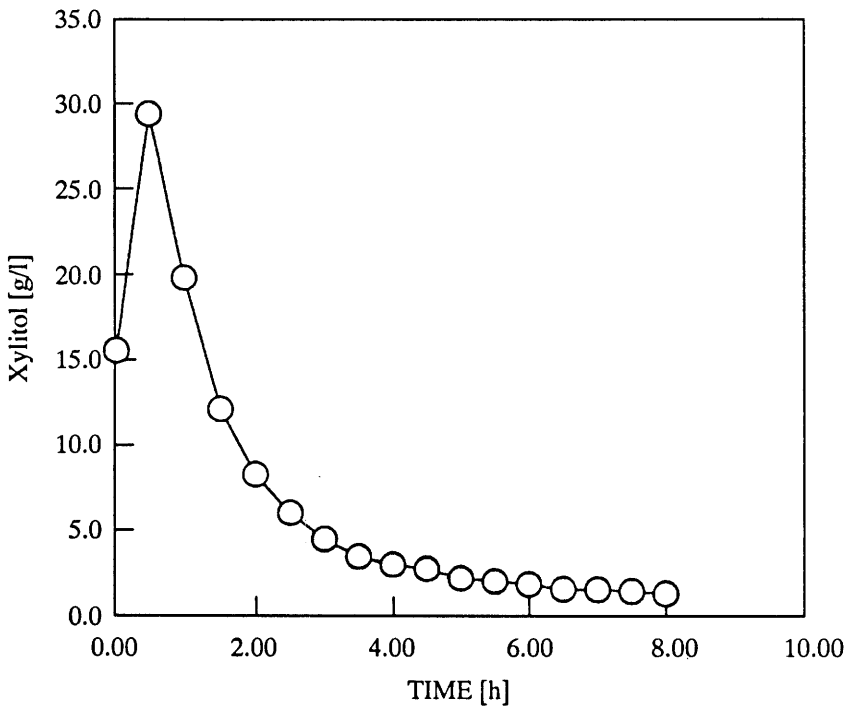


Figure 8 Desorption of xylitol from packed bed column of granular activated charcoal with ethanol (F = 10 ml/min).

that surface diffusion coefficient, D_s depends on the amount of adsorbed (q). This dependence of D_S on q was explained by a decrease of adsorption energy (E) with increasing q. The relation between D_S and q was derived thermodynamically for Langmuir isotherm system as shown in Eq. (10) with $D_S^0 = 0.7911 \times 10^{-8}$ m²/min and k = 5.849. Therefore the external mass transfer resistance in the stirred tank has a large influence on the adsorption rate in the finite bath adsorption (Muraki *et al.*, 1982).

In case of the fixed-bed adsorption, a perfect mixing model rather than a diffusion model could verify the experimental result quite well (Figure 6). However, this proposed model gave no breakthrough time of the packed bed column by changing the flow rates or the bed lenghts (Figure 7). Only different saturation times were clearly realized. The more experiments with different flow rates and bed lenghts should be investigated to prove the absolute validity of a perfect mixing model under such range of this work. Moreover, modeling of xylitol desorption from packed bed column have to be eventually evaluated. Therefore, the results obtained may be used directly for the design of fixed-bed column for recovery of xylitol from fermentation process.

RECOMMENDATION

The study of xylitol separation using activated charcoal has indicated that kinetic of Langmuir isotherm could be applied for xylitol adsorption phenomenon in either batch or packed bed column under conditions specified here. The exploitation of packed bed column of activated charcoal needs further investigations focusing on desorption of xylitol by ethanol. Furthermore, a process for adsorption and desorption of xylitol utilizing packed bed column of activated charcoal have to be optimized for fermentation broth containing xylitol and other components. Finally, the resulting operation of xylitol recovery by activated charcoal shall be connected to high dense culture with hollow fiber module in order to succeed the whole microbial process for xylitol production.

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ABBREVIATIONS

av	specific surface area of activated charcoal defined as the surface area per unit volume of activated charcoal	[kg/m³]
C_L	xylitol concentration in the solution	[kg/m³]
C_{L0}	initial concentration of xylitol in the solution	[kg/m³]
C_{LE}	equilibrium concentraiton of xylitol in the particles	[kg/m³]
C_{PO}	initial concentration of xylitol in the particles	[kg/m³]
D_L	axial dispersion coefficient	[m³/s]
D_S	surface diffusion coefficient	[m²/min]
D_S^0	surface diffusion coefficient defined by Eq. (10)	[m²/min]
E	adsorption energy	[kJ/mol]
K	Langmuir constant	[m³/kg]
K'	separation factor defined by Eq. (5)	[-]
K_F	overall mass transfer coefficient	[m/s]
k	constant defined by Eq. (10)	
k'	coefficient Langmuir isotherm defined by Eq. (6)	[m³/kg]
Q_{max}	maximum xylitol uptake	[kg/kg]

q	xylitol uptake	[kg/kg]
q_o	amount adsorbed at C_{LO}	[kg/kg]
q_∞	equilibrium amount adsorbed at C_{LE}	[kg/kg]
R	particle radius	[cm]
r	radial position within the particle	[cm]
t	time	[min]
t_b	breakthrough time	[min]
t_s	saturation time	[min]
u	intergranular fluid velocity	[m/s]
V_L	liquid volume	[m^3]
W_S	weight of particles	[kg]
z	distance measured from input face of bed	[m]
	bed lenght	[m]
ε	void fraction in the bed	[-]
γ	bulk density of activated charcoal	[kg/m^3]
ρ_p	density of particle	[kg/m^3]

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