Cephalosporin C 의 흡착평형 및 파과곡선에 미치는 pH 의 영향

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Effect of pH on Adsorption Equilibrium and Breakthrough Curves for cephalosporin C

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INTRODUCTION

Since cephalosporin C can exist as cations, neutral and anions depending upon the solution pH, ion exchange resins offer variety of oppertunities. However nonionic resins rather than ion exchangers have been widely used for the separation of cephalosporin C because of easy elution and regeneration steps in industrial cyclic operation [1]. One of the key separation problems is how to get rid of penicillin N coexisted in broths. Penicillin N can be removed at low pH (about pH 3.0) due to the low stability in acid. Therefore, it is essential to investigate the effect of pH on adsorption capacity and behavior in a fixed bed charged with a nonionic polymeric resin.

In order to understand the effect of pH systemetically, the equilibrium amounts of cephalosporin C were measured in terms of solution pH. Since the concentrations of individual ions can be known from the solution dissociation equilibria at a given solution pH and concentration, isotherms for different ions could be obtained. The dynamic behavior of cephalosporin C in a fixed bed can be considered as a compatitive adsoption of ion according to the solution pH.

ADSORPTION MODEL IN A FIXED BED ADSORBER

By taking into account the dissociation equilibria, the concentrations for ions can be determined [2]. The total concentration, C_T, in solution is given by

$$C_T = C^+ + C^\pm + C^- + C^{2-} \tag{1}$$

where

$$C^+ = \frac{C_T}{\left(1 + \frac{K_1}{C_{H^+}} + \frac{K_1K_2}{C_{H^+}^{\ 2}} + \frac{K_1K_2K_3}{C_{H^+}^{\ 3}}\right)} \tag{2}$$

$$C^- = \frac{C_T}{\left(1 + \frac{C_{H^+}}{K_2} + \frac{C_{H^+}^{\ 2}}{K_1K_2} + \frac{K_3}{C_{H^+}}\right)} \tag{3}$$

$$C^{2-} = \frac{C_T}{\left(1 + \frac{C_{H^+}}{K_3} + \frac{C_{H^+}^{\ 2}}{K_2 K_3} + \frac{C_{H^+}^{\ 3}}{K_1 K_2 K_3}\right)} \tag{4}$$

In the present model, the axial dispersion in the external fluid phase, the mass transfer resistance in the liquid film surrounding the particles and the diffusion inside the particles are included. In the formulation of the model, the following assumptions are considered: The system is isothermal, the radial concentration gradients are neglected and the physical properties are unchanged. The governing equations can be written as follows. The mass balance equation for the solute in the solid phase is given by:

$$\frac{\partial q_i}{\partial t} = D_{si}\left(\frac{\partial^2 q_i}{\partial r^2} + \frac{2}{r}\frac{\partial q_i}{\partial r}\right) \tag{5}$$

The mass balance in the external fluid phase can be written as:

$$-D_z \frac{\partial^2 C_i}{\partial z^2} + \frac{\partial \upsilon C_i}{\partial z} + \frac{\partial C_i}{\partial t} + \frac{1-\varepsilon_b}{\varepsilon_b}\frac{\partial q_i}{\partial t} = 0 \tag{6}$$

The fluid concentration is related to the particle concentration through the multicomponent equilibria. IAST(Ideal Adsorbed Solution Theory) is used for the determination of the surface concentrations.The set of eqs. (5) and (6) and these boundary conditions are reduced to a set of first order ordinary differential equations by orthogonal collocation on finite element method [3]. The resultant ordinary differential equations were integrated by LSODI as an integrator.

EXPERIMENTAL

A zink form cephalosporin C obtained from Sigma (U.S.A) was uesd as a standard material and, in all subsequent experiments, the sodium form manufactured by Cheil Food & Chemicals Inc. (Korea) were used. Both cephalosporin C were used without further purification. HCl solution were used to adjust the solution pH. The nonionic polymeric sorbent used in this study was a macroreticular and spherical sulfonated polystyrene resin cross-linked with DVB(divinylbenzene), SP850, which was manufactured by Mitzubishi Co. (Japan). The physical properties are summarized in Table 1.

Equilibrium data were taken by introducing a given amount of sorbent into a mixed solution with an excess volume , 50 ml, of a cephalosporin C solution containing 1-100 mol/m^3 at 25°C, shaking in a constant temperature incubator for 5hrs which is enough to reach equilibrium and measuring the adsorbate concentrations remained in the solution by UV spectrometry at 260nm. The hydrogen concentration was measured by pH meter (model Fisher 420). Single-species adsorption was carried out in a fixed-bed adsorber which was made of a glass column of 2cm diameter and 20cm long packed with resin particles. The column was lined with a water jacket to maintain the uniform column temperature. The flow rate was regulated by a precision FMI pump(model RHOCKE). The solution was introduced downward into the column. To prevent channeling and to enhance distribution of the solution through the column, the two layers of small glass beads were packed in the top and bottom region of the column.

RESULTS AND DISCUSSION

As illustrated in Fig.1, adsorption amounts increased with decreasing solution pH. The concentations and adsorbed amont of each ions can be determined from the solution Table 1. dissociation equilibria. As listed in Table 2, the values of the Langmuir isotherm parameters for each ion were obtained by minimizing the mean percent deviation between experimental and predicted values of amounts adsorbed. Fig. 2 show the adsorption breakthrough of cephalosporin C onto SP850 in fixed beds in terms of solution pH. The adsorption equilibrium and dynamic behaviors were quite sensitive to the change in the solution pH. The adsorption model succesfully simulates the experimental result in a fixed bed adsorber. However, there were some deviation at low pH.

Table 1. Physical Properties of Polymeric Sorbents

Adsorbent	SP850	Unit
Chemical structure	Polystyrene	-
Particle size	200/750	μm
Particle density	457	m^3/kg
Packing density	290	m^3/kg
Particle porosity	0.55	-
Packing porosity	0.37	-
Moisture content	52	%
Surface area	1,000	m^2/g
Ave. pore diameter	38.1	A
Specific gravity	1.01	-

Table 2. Langmuir Isotherm Parameters

Ions	qm	b
Positive	2.699	0.048
Neutral	0.584	0.382
Negative	0.965	0.011

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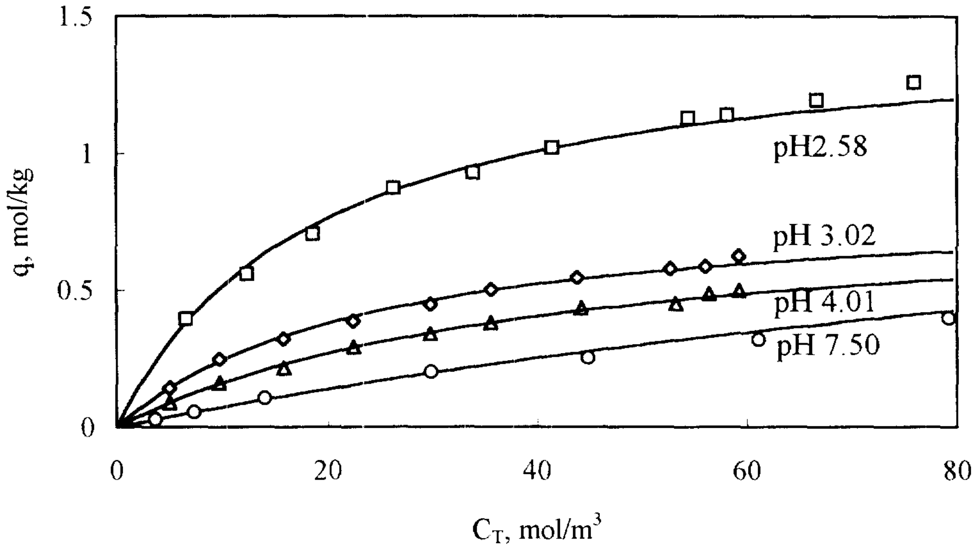

Figure 1. Equilibrium isotherm of cephalosporin C in terms of solution pH.

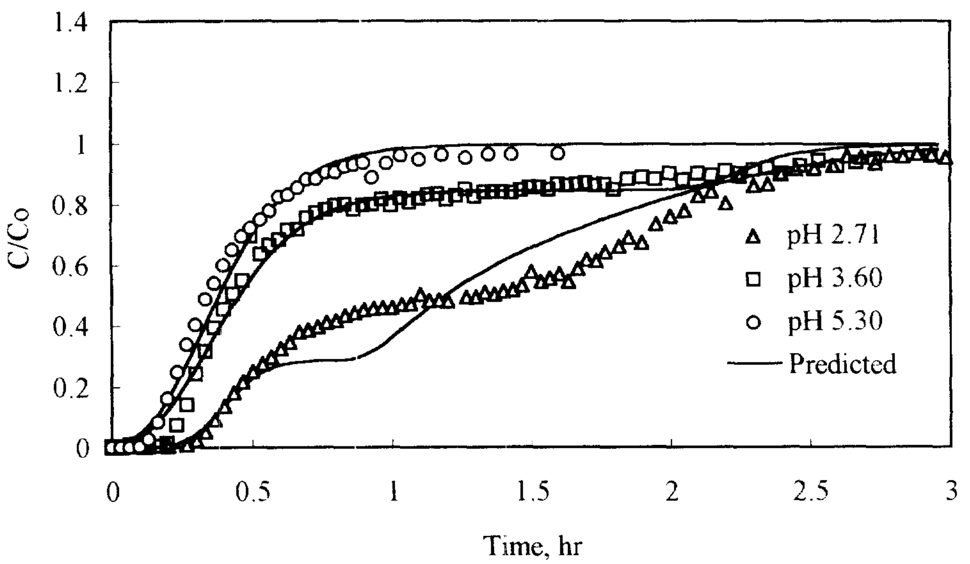

Figure 2. Experimental results and model predictions of breakthrough curves.