

Unusual Adsorber Dynamics Due to S-Shaped Equilibrium Isotherm

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Abstract—A fixed bed adsorption study has been performed to investigate the effect of S-shaped (Type V) equilibrium isotherm on the breakthrough patterns. The adsorption breakthrough data of benzene vapours on dealuminated zeolite Y were collected by using a lab-scale fixed bed apparatus. It was found that the adsorption system, at influent concentrations from 100 to 5,000 ppm at 303 K, yields breakthrough curves of unusual shapes. A mathematical model was applied to predict the complex breakthrough patterns at various conditions. The experimental and modelling results suggest that the unusual breakthrough curve is due to the basic shape of the equilibrium isotherm.

Key words: Fixed Bed, Adsorption, S-Shaped Isotherm, Breakthrough Curve, Modelling

INTRODUCTION

Fixed bed adsorption is popularly adopted for separation and purification problems in engineering applications. The performance of a fixed bed unit is often evaluated by examining the dynamic concentration history at the bed exit. This concentration vs. time history is frequently referred to as a *breakthrough curve*. It is well known that the adsorber dynamics depends on several factors such as bed geometry, adsorption system, operating conditions, heat and kinetic effects, and adsorption equilibrium relationships. Among them, the thermodynamic equilibrium properties and the kinetic information have been generally regarded as the most important design factors for an adsorption process. In general, such information should be incorporated into a mathematical model, and the resulting numerical or analytical solution is commonly used as a predictive tool for process design.

It has been realised that the shape of the equilibrium isotherm greatly influences adsorber dynamics. Usually, experimental studies on the effects of the shape of the equilibrium isotherm on the column dynamics have been limited to linear and favourable systems, and rarely to unfavourable systems. For more complicated equilibrium relationships, which are distinguishable as Type IV or V, however, very few studies were done before Park and Knaebel [1992]. They studied an adsorption system of water vapour and silica gel, which exhibits Type IV isotherm, and found the equilibrium isotherm and heat effects can cause unusual dynamics in fixed bed adsorber, while the mass transfer effects were relatively small.

In a previous study [Yun et al., 1998], the adsorption systems of gaseous solvents-DAY (dealuminated zeolite Y) were found to exhibit unusual S-shaped equilibrium isotherms. Based on the previous results, an elementary study on adsorption dynamics of solvents in fixed DAY beds has been carried out. The basic purposes of this study are to experimentally investigate the breakthrough pattern for an S-shaped equilibrium system under a re-

stricted condition that thermal effects may be neglected, and to predict the dynamic behaviour by a mathematical model.

In the present study, an interesting dynamic behaviour was observed in the benzene-nitrogen-DAY system. For this system, the breakthrough patterns of the adsorber were strongly influenced by the influent benzene concentration. In the case of the low benzene concentration ranges (unfavourable region in the S-shaped isotherm), the effluent concentration profiles showed a typical proportional pattern. On the other hand, in the relatively high concentration ranges (favourable region), the effluent concentration profiles tended to produce a constant pattern. In addition, a very complicated breakthrough pattern was observed in the intermediate region (between favourable and unfavourable regions). This paper presents the experimental and modelling results on unusual adsorber dynamics, which are mainly due to the S-shaped isotherm.

EXPERIMENTAL

A laboratory scale fixed bed adsorption unit was used to study adsorber dynamics in an isothermal condition. Dealuminated zeolite Y, designated as DAY by Degussa AG, was used as the adsorbent for the present study. The samples were crushed into 12-14-mesh to ensure a uniform particle size before introducing to the adsorption column. Table 1 lists properties of packing charac-

Table 1. Properties of packing characteristics and column used

Adsorbent	DAY (Degussa AG) 12-14 mesh
Effective particle diameter, cm	0.154
Particle porosity	0.350
Bed packing density, g/cm ³	0.502
Bed void fraction	0.676
Packing amount, g	13.16
Column length, cm	20.0
Column I.D., cm	1.82
Column O.D., cm	2.20

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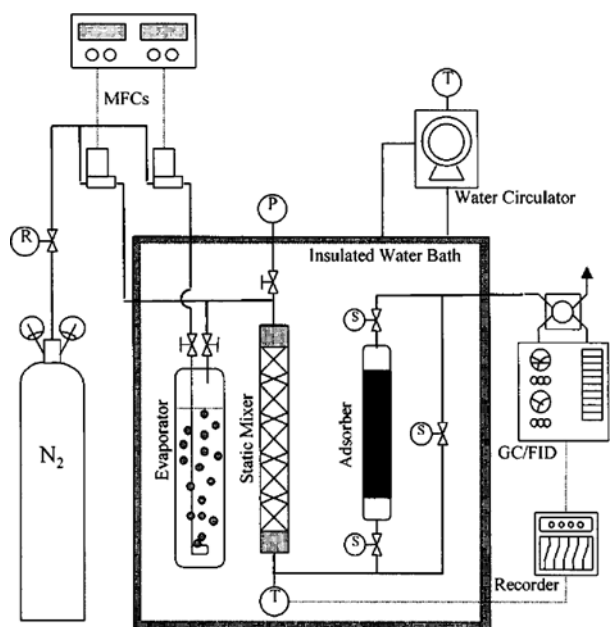


Fig. 1. A schematic diagram of the experimental apparatus used.

teristics and column used. Besides, the physical properties of DAY can be found elsewhere [Yun et al., 1998].

Fig. 1 shows a schematic diagram of the experimental apparatus used. The nitrogen gas line was divided into two branches. One is for pure nitrogen gas as a carrier, and the other is connected to a benzene evaporator. In the method, a part of the nitrogen gas was fed to the evaporator to load benzene, and was mixed with the pure nitrogen gas stream. To ensure homogeneous mixing, the static mixer was installed at the inlet section of the adsorption column. All the gas flow rates were adjusted and metered by mass flow controllers with a readout power supply. The system temperature was controlled by refrigerating/heating water circulator and its accuracy was ± 0.02 °C at 303 K. The concentration of benzene in the feed was determined by controlling each mass flow controller, and was identified several times by a gas chromatograph equipped with flame ionisation detector before inlet flow to the adsorption column. During the adsorption, the concentration history at the bed exit was monitored by the gas chromatograph with an automatic 6-port valve. After each adsorption experiment, a saturated adsorption column was regenerated for the next experimental run by admitting the pure nitrogen flow at 474 K for 12 h.

FIXED BED MODEL

The system considered in this study is that of an adsorber packed with porous adsorbent particles through which an inert carrier flows at a steady state. The basic assumptions made for the present model are as follows:

- The system is isothermal.
- Two fluid phase species, comprising an ideal gas mixture, are present.
 - Only one species is adsorbable and this exists at a trace level.
 - The system pressure, gas flow rate, and the feed concentration are assumed to be constants.

- The linear driving force (LDF) approximation represents the mass transfer resistances between fluid and the solid phases.
- The physical properties of the fluid phase are assumed to be those of the carrier gas.

Based on the above assumptions, a mass balance for the adsorbed species in fixed bed may be written as:

$$\frac{\partial y}{\partial t} - D_L \frac{\partial^2 y}{\partial z^2} + u \frac{\partial y}{\partial z} + \frac{1 - \epsilon RT}{\epsilon P} p_p \frac{\partial n}{\partial t} = 0 \quad (1)$$

The mass balance within the solid phase may be approximated as the fluid phase linear driving force equation.

$$\frac{\partial n}{\partial t} - \frac{\alpha P}{\rho_p RT} K_s (y - y^*) = 0 \quad (2)$$

The boundary conditions at the bed entrance and the bed exit are:

$$D_L \left. \frac{\partial y}{\partial z} \right|_{z=0} = -u (y|_{z=0} - y|_{z=0}^*) \quad (3)$$

$$\left. \frac{\partial y}{\partial z} \right|_{z=L} = 0 \quad (3)$$

And the associated initial conditions for the clean beds are:

$$\begin{aligned} y(z, 0) &= y_0 = 0 \\ n(z, 0) &= n_0 = 0 \end{aligned} \quad (4)$$

In the fluid phase linear driving force model, the driving force is the concentration gradient between the fluid phase and the equilibrium fluid phase corresponding to the solid phase. An effective overall mass transfer coefficient could be derived as follows [Huang and Fair, 1988]:

$$\frac{1}{K_s} = \frac{1}{k_f} + \frac{R_p}{5D_e} \quad (5)$$

where k_f is the film mass transfer coefficient and D_e is the effective intraparticle diffusion coefficient, which includes the pore diffusivity and the surface diffusivity.

Because of the low Reynolds number region covered in the present study, the Petrovic and Thodos correlation is used to calculate the film mass transfer coefficient k_f [1968]. Therefore, the effective diffusion coefficient is only an adjustable parameter in this study and it can be obtained simply by the parameter estimation using the experimental data.

To represent the S-shaped equilibrium relationship for benzene-DAY system, Martinez and Basmadjian's adsorption isotherm [1997] that contains five adjustable parameters was used and the parameter values can be found elsewhere [Yun et al., 1998].

$$Py^* = M_0 \exp(-Q/kT) \frac{\theta}{(1-\theta)^2} \quad (6)$$

where $\theta = n/n^*$ and $Q = \chi - rW\theta$.

The system of model equations to be solved consists of the governing equation and the mass transfer equation as well as the equilibrium isotherm. Although the model equation included the axial dispersion coefficient, plug flow was approximated by assigning a very large value to the Peclet number (uL/D_L). This is because

the effect of axial dispersion is negligible in a small column and the model with the second derivatives can give more stable numerical results. The coupled PDEs [Eqs. (1) and (2)] were first reduced to a set of ODEs by the method of lines technique, and resultant ODEs were integrated with respect to time by using the subroutine DIVPAG in IMSL.

RESULTS AND DISCUSSION

Fig. 2 shows adsorption equilibrium isotherm for benzene on DAY at 303 K. The original experimental isotherm data can be found elsewhere [Yun et al., 1998]. As seen, the adsorption isotherm exhibits S-shape isotherm in the low concentration range and it could be classified as Type V according to the classification of Brunauer et al. [1940]. As indicated in Fig. 1, the adsorption isotherm begins with a linear region, and is followed by the unfavourable and intermediate regions, in sequence, and finally approaches to the favourable region. Such complex equilibrium behaviour may be explained by several reasons such as multilayer sorption, pore filling, and the nature of the solid surface [Park and Knaebel, 1992].

To investigate the effect of S-shaped equilibrium isotherm on breakthrough behaviour, several fixed bed experiments were performed at various influent benzene concentrations. All experiments were carefully conducted with the equilibrium conditions indicated in Fig. 2 (A to F). Typical experimental results at each condition are shown in Fig. 3, along with the prediction results. It is evident that the influent concentration greatly influences the shape of the

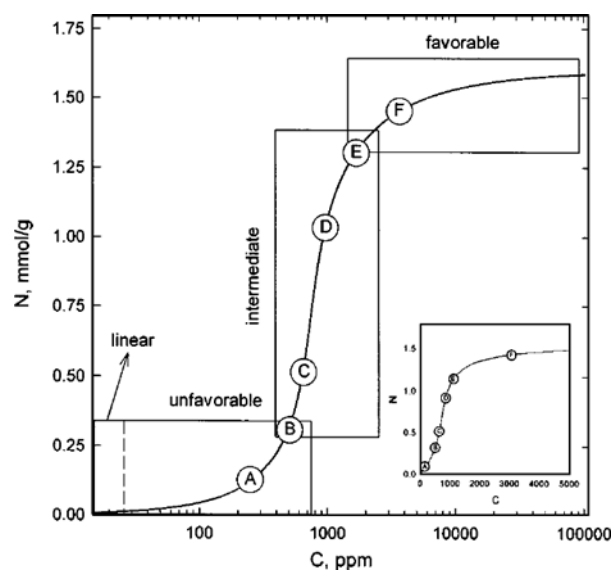


Fig. 2. Adsorption equilibrium isotherm of benzene on dealuminated zeolite Y (DAY) at 303 K.

breakthrough curve. At the lowest influent concentration condition A ($C_0=250$ ppm), the breakthrough curve forms a constant pattern in shape, and the experimental data are represented well by the model prediction. At the unfavourable condition B ($C_0=500$ ppm), a proportional breakthrough pattern is observed and model prediction gives good agreement with the data. At the intermediate condition C ($C_0=780$ ppm), a highly developed proportional break-

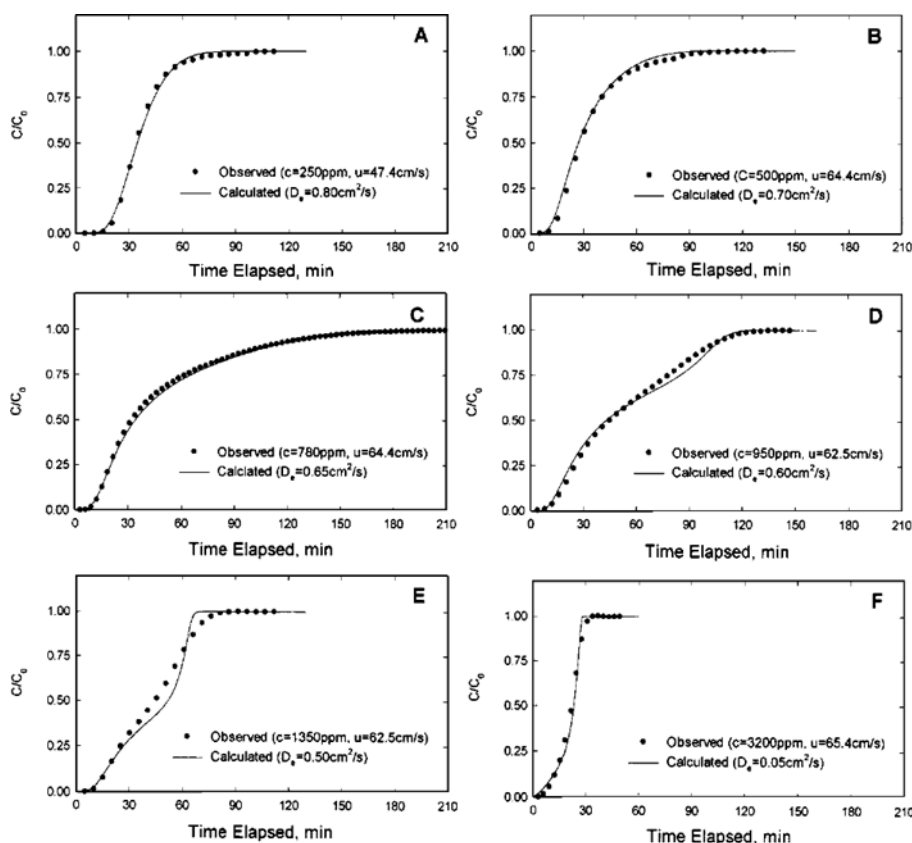


Fig. 3. Experimental and predicted breakthrough curves at various influent concentrations.

through curve is found. Park and Knaebel [1992] reported a similar result in the system of water vapour-silica gel, which exhibits Type IV equilibrium isotherm. They described such a long-tailed breakthrough curve as a combination of constant and proportional patterns. Again, the model predicts such behaviour very well. Thereafter the breakthrough curves show more complicated behaviours at the conditions D ($C_0=950$ ppm) and E ($C_0=1,350$ ppm). Park and Knaebel [1992] also found the similar results in their system and defined such behaviour as “dual-shock wave” or “dual-constant pattern”. For these conditions, however, the model failed to predict the experimental data accurately. At the highest experimental concentration F ($C_0=3,200$ ppm), the breakthrough curve is started with a proportional pattern, and the saturation seems to

occur abruptly. Obviously, the model still expresses such breakthrough behaviour reasonably.

To understand these unusual breakthrough behaviours, several calculations were performed with a bed of three times longer than an experimental bed, while other input variables follow those of experimental conditions. Fig. 4 shows theoretical concentration profiles in the bed for the previously mentioned conditions A, C, D, and F. At condition A, the propagation profile tends to exhibit a constant pattern along the bed at early stage; however, the profile becomes broader slowly as the concentration front moves toward the outlet at a steady velocity. As the influent concentration increases, the profile in the bed exhibits a more significant proportional pattern as shown in the result at condition C. In the beginning, the concentration profiles show nearly exponential decay, and then become broader very much as they propagate. At the condition D, the concentration profile starts with initial patterns similar to that of condition C, but soon evolves to a constant pattern (shock wave), which expands throughout the higher concentration range, instead of maintaining a proportional pattern. However, any significant second constant pattern (second shock wave) is not found. At the highest concentration condition F, the concentration profile initiates with the exponential decay, but a constant pattern appears immediately and this pattern is hardly maintained throughout the bed. In the meanwhile, a proportional pattern is also found at low concentration range and this does not dissipate through the entire bed.

The effect of gas flow rate on the breakthrough curve was also examined at the intermediate concentration condition D and the results are shown in Fig. 5. Although the model prediction accuracy is not excellent, it could be clearly stated that the basic shape of a breakthrough curve is not influenced by the bulk flow rate.

CONCLUSION AND FUTURE WORKS

In this study, the effects of the S-shaped equilibrium isotherm (so-called Type V) on breakthrough curves are investigated experimentally. Several fixed bed experiments were carefully conducted using the lab-scale isothermal equipment. From the results, various breakthrough patterns were observed at different influent concen-

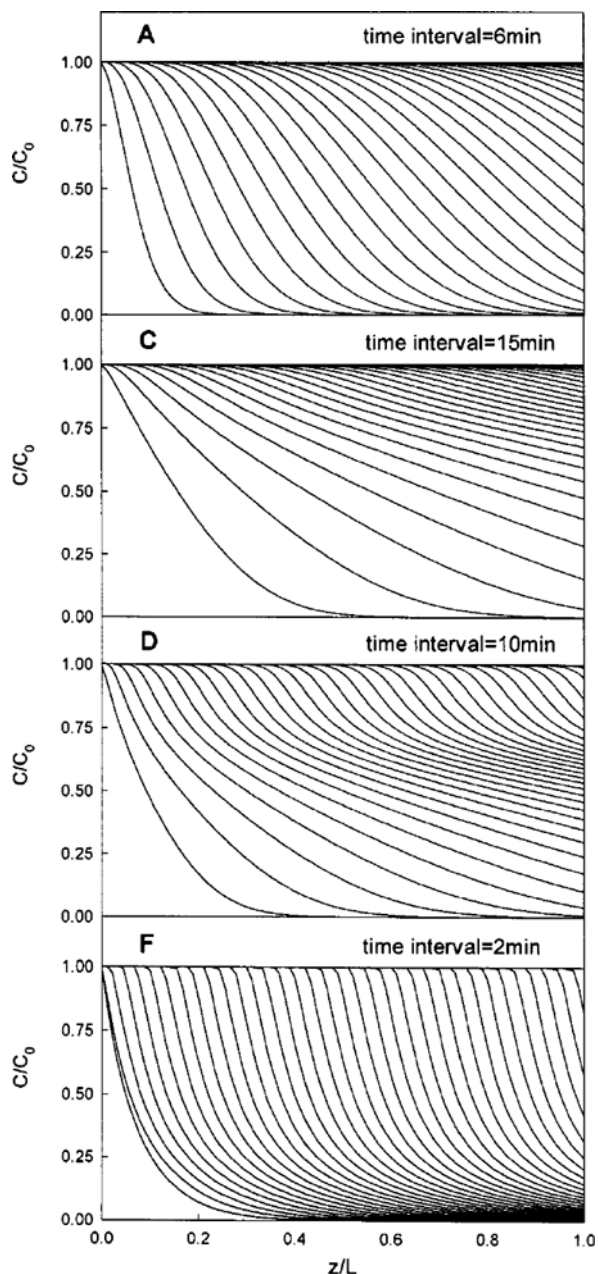


Fig. 4. Concentration profiles in the bed at various influent concentrations.

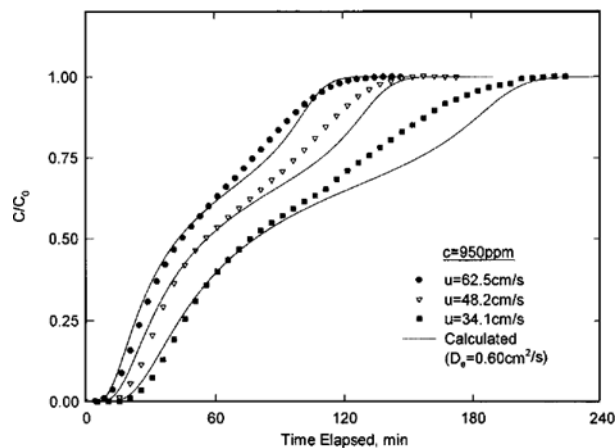


Fig. 5. Effect of bulk gas flow rate on breakthrough pattern at the intermediate condition.

tration conditions. A fixed bed model was used to elucidate the causes of the unusual breakthrough patterns and to predict the experimental data. The experimental and modelling results showed that the unusual breakthrough behaviour is mainly due to the shape of the equilibrium isotherm.

As Park and Knaebel [1992] realised in a non-isothermal study, the adsorption equilibrium properties and their performance on adsorption dynamics are strongly connected with temperature effects, and some of the effects (e.g. the heats of adsorption and desorption) may be unavoidable in an actual process. To understand the principles of unusual adsorption dynamics, therefore, more experimental and theoretical efforts are necessary.

NOMENCLATURE

D_e	: effective diffusion coefficient [cm ² /s]
D_L	: axial dispersion coefficient [cm ² /s]
K_e	: effective mass transfer coefficient [cm/s]
k_f	: film mass transfer coefficient [cm/s]
n	: moles adsorbed [mmol/g]
P	: pressure [kPa]
R	: gas constant
R_p	: particle radius [cm]
T	: temperature [K]
t	: time

u	: interstitial velocity [cm/s]
y	: gas phase composition
z	: axial distance coordinate

Greek Letters

α	: geometric surface area of spherical pellet [1/cm]
ϵ	: bed void fraction
ρ_p	: particle density [g/cm ³]

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