

How Favorable Isotherm Is Favorable in Pressure Swing Adsorption?

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ABSTRACT

A favorable isotherm open to the right to some extent is better than a linear isotherm to give shorter column height in pressure swing adsorption(PSA). We face to a problem how favorable isotherm is actually favorable in PSA operation. The purpose of this paper is to propose how to construct such a custom made isotherm which optimizes the PSA processes. The PSA model was much simplified to approach this complicated problem. The first simplification is a method called the short cycle time approximation, in which the time-dependent partial differential equations were simplified to steady state equations for a short half cycle time. As the next simplification, the HETP(height equivalent to a theoretical plate) concept was applied to predict the total column height of PSA. The total height was found to be the sum of the reciprocal of average gradient of adsorption isotherm weighted with a ratio of gas velocity in desorption step to that in adsorption step. By use of this result, the most “favorable” isotherm to give the shortest column height was constructed by increasing the gradient of isotherm in the next stage by a factor of square root of the velocity ratio. Thus obtained isotherm was better to shorten the column height than any available isotherms even with the best parameters.

INTRODUCTION

A nonlinear adsorption isotherm open to the right is called “favorable” isotherm. It is truly favorable in the case of a fixed bed operation since the column height gets shorter when the isotherm is as “favorable” as possible. The situation is more complicated in the case of pressure swing adsorption(PSA). PSA is a cyclic operation of adsorption and desorption, and the “favorable” isotherm is unfavorable actually in desorption step while it is favorable in adsorption step. Due to this type of conflicting effects, we face to a problem how “favorable” isotherm is actually favorable for PSA operation. Such an optimization may be carried out by

selecting the best parameter of available isotherms, e.g. the κ value in Freundlich isotherm $q=ac^{1/\kappa}$. However, we are seeking the further better isotherm which cannot be expressed in terms of available isotherms even with the best parameter values. The purpose of this paper is to propose how to construct such a custom made isotherm rather than ready mades.

The PSA model was much simplified to approach this complicated problem. The first simplification is a method called the short cycle time approximation. Behavior in PSA is different from the conventional counter-current contactors such as in distillation, gas absorption, etc. since it is a time dependent cyclic operation. However, when adsorption and desorption steps are repeated with a short cycle time in a bed of high capacity of adsorption under limited rate of intraparticle diffusion, we expect that the profile of amount adsorbed is confined just in the vicinity of the particle surface and the average amount adsorbed remains substantially unchanged during such a short cycle time. This limiting situation may lead to steady state solutions of PSA dynamics, which have been investigated in terms of the short cycle time approximation[1-3] and verified experimentally for dehumidification from air[4, 5] and CO₂ removal[6].

The other simplification was an introduction of HETP(Height equivalent to a theoretical plate) concept. Component separation is processed usually by contacting two different phases in stage-wise contactors or differential contactors. Equilibrium or ideal stage is assumed in design of the stage-wise contactor when two streams leaving the particular stage are in equilibrium. A differential contactor such as a packed bed distillation column does not have such a discrete stage but height equivalent to a theoretical plate(HETP) has been introduced to design a differential contactor in a way analogous to a stage-wise contactor. An HETP is defined as the length across which two leaving streams are in equilibrium. We proposed that HETP can also be defined in PSA for the limiting case approaching the steady state and developed a new design method for PSA by applying the HETP concept[7].

The design method with these simplifications is probably the simplest since calculus is not involved and all we need is just algebra. The resulting optimization problem, which

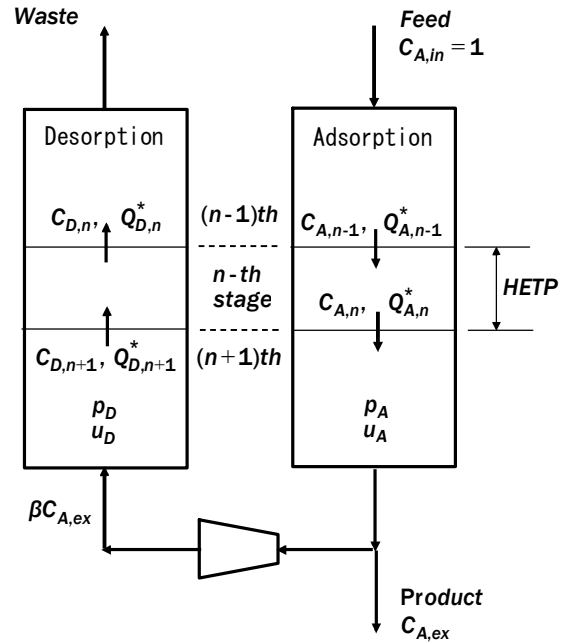


Fig.1 Schematic diagram of PSA and relevant nomenclature

usually involves the calculus of variations of an infinite number of continuous variables, is replaced by the conventional differentiation of finite number of discrete variables. In the following discussion, the process is limited to the removal of a trace component in a simple two-step two-column PSA, and concentration C and amount adsorbed Q are expressed in dimensionless terms relative to the condition of feed gas, i.e. $C=c/c_{A0}$ and $Q=q/m_{0cA0}$.

HETP(HEIGHT EQUIVALENT TO A THEORETICAL PLATE)

Equilibrium stage (or ideal stage) is familiar to chemical engineers. Two streams leaving the stage are assumed to be in equilibrium. This concept was extended to a differential contactor having no discrete stage and HETP was defined as a distance across which two streams are in equilibrium. Gas-liquid equilibrium is straightforward as in the case of distillation. When PSA is considered in analogy to distillation, the high pressure side corresponds to liquid and the low pressure side to vapor phase. Purge to a low pressure column has the same function of reboiler and so purge may be called a stripping reflux. Equilibrium between phases is realized in PSA by the fact that concentration under column pressure is the same between adsorption and desorption steps but not the adsorption equilibrium between gas and adsorbent. Thus the equilibrium condition at the exit of the n-th stage is given as

$$C_{D,n} = C_{A,n}, Q_{D,n}^* = Q_{A,n}^* \quad (1), (2)$$

in reference to Fig.1 and is designated with A-line in Fig.2 in which C_D, Q_A^* and Q_D^* are related to C_A . When C_D is related to C_A at the same position of the column, we have a mass balance equation or an operating line

$$C_{D,n} = \beta C_{A,ex} + (1/\gamma)(C_{A,n-1} - C_{A,ex}) \quad (3)$$

which is designated with D-line in Fig.2. Thus the number of equilibrium stage is calculated simply by a familiar step-wise drawing between the A- and D- lines as shown in Fig.2. Since triangles formed between two lines are all

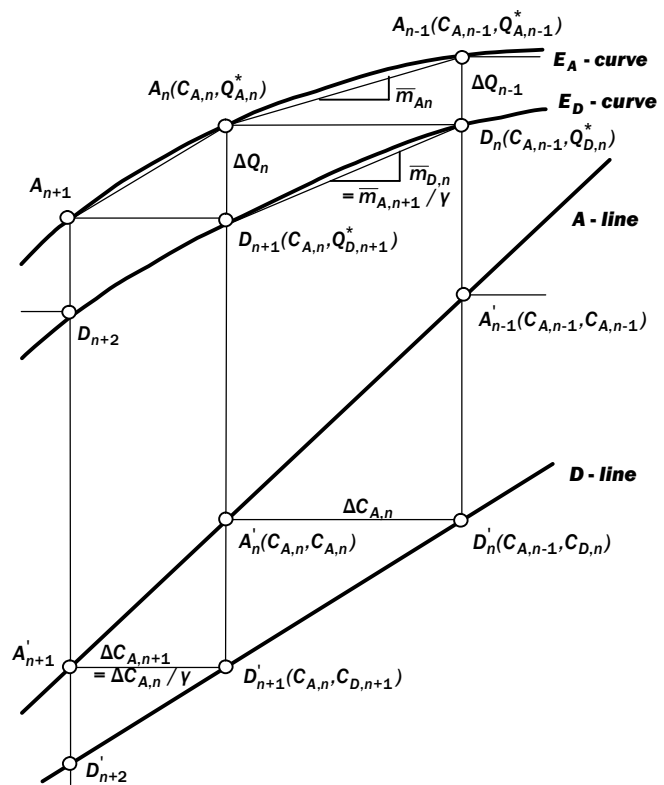


Fig.2 Detailed diagram to calculate the HETP

similar figures, the concentration $C_{A,n}$ and the difference $\Delta C_{A,n} (=C_{A,n-1}-C_{A,n})$ at the n-th stage is given by

$$\Delta C_{A,n} = \Delta C_{A,n-1} / \gamma \quad (4)$$

$$C_{A,n} = 1 - \Delta C_{A,1} (1 - \gamma^n) / (1 - \gamma^{-1}) \quad (5)$$

in which the first difference $\Delta C_{A,1}$ is given by

$$\Delta C_{A,1} = 1 - C_{A,1} = 1 - C_{D,1} = (1 - \beta C_{A,ex}) - (1 - C_{A,ex}) / \gamma \quad (6)$$

When adsorption isotherm (E_A-curve) is given in the same figure, equilibrium amount adsorbed $Q^*_{A,n}$ at n-th stage in adsorption step can be read easily. Amount adsorbed $Q^*_{D,n}$ in desorption step is equal to $Q^*_{A,n}$ at the same stage in adsorption step by Eq.(2). Therefore, amount adsorbed in desorption step (E_D-curve) is obtained by shifting the amount adsorbed in adsorption step to one stage right. Finally, the driving force $\Delta Q = Q_A^* - Q_D^*$ is given by a distance between E_A-curve and E_D-curve. HETP of the n-th stage L_n can be evaluated in terms of the corresponding number of mass transfer units NTU_n by integration of the reciprocal of driving force over the stage in the frame of the short cycle time approximation[2].

$$NTU_n \equiv \frac{K_A a m_0 L_n}{u_A} = \int_{C_n}^{C_{A,n-1}} \frac{2dC_A}{Q_A^* - Q_D^*} \quad (7)$$

We are required to integrate Eq.(7) for n-th stage from $C_{A,n-1}$ to $C_{A,n}$. This kind of integration by stage to stage may be the most exact method to evaluate the HETP. However, calculation will be simplified when the integral is replaced by a suitable average driving force.

When the isotherm is linear, the integral is given by a log mean of driving forces at both ends of the n-th stage ΔQ^*_n and ΔQ^*_{n-1} . However, any kind of average does not make much difference in result if two values are not much different. We are much interested in a harmonic mean for simplicity in further treatment.

$$\begin{aligned} NTU_n &= \frac{C_{A,n-1} - C_{A,n}}{Q^*_{A,n-1} - Q^*_{D,n}} + \frac{C_{A,n-1} - C_{A,n}}{Q^*_{A,n} - Q^*_{D,n+1}} = \frac{C_{A,n-1} - C_{A,n}}{Q^*_{A,n-1} - Q^*_{A,n}} + \frac{C_{A,n} - C_{A,n+1}}{Q^*_{A,n} - Q^*_{A,n+1}} \times \gamma \\ &= \frac{1}{m_{A,n}} + \frac{\gamma}{m_{A,n+1}} \end{aligned} \quad (8)$$

in which $m_{A,n}$ is an average gradient of adsorption isotherm, i.e. the slope of a line A_nA_{n-1} in Fig. 2. Thus, HETP can be obtained arithmetically from a weighted average of reciprocals of average gradient of adsorption isotherm.

In this procedure we do not need any integration but all we need is just an addition. The basic concept of the HETP method is based on the short cycle time approximation[1,2], of which the accuracy was discussed in detail. The controlling

parameter for accuracy is $\lambda = K_A a t_c / \rho_s$ and a good accuracy holds for $\lambda < 1$ by the short cycle time approximation. The same criterion is applied to the present HETP method.

OPTIMUM ADSORPTION ISOTHERM

The total height of the column L_T is just a sum of each HETP given by Eq.(8)

$$NTU_T \equiv \frac{K_A a m_0 L_T}{u_A} = \sum_{n=1}^N NTU_n = \frac{1}{m_{A,1}} + (1 + \gamma) \sum_{n=2}^N \frac{1}{m_{A,n}} + \frac{\gamma}{m_{A,N+1}} \quad (9)$$

The total difference of amount adsorbed ΔQ_T^* through the whole column is

$$\Delta Q_T^* = 1 - Q_{D,N}^* = 1 - Q_{A,N+1}^* = \sum_{n=1}^{N+1} m_{A,n} \Delta C_{A,n} = \Delta C_{A,1} \sum_{n=1}^{N+1} m_{A,n} / \gamma^{n-1} \quad (10)$$

The optimization of the isotherm is equivalent to determining the (N+1) variables of $m_{A,1}$ to $m_{A,N+1}$ so that the total column height L_T or the value of NTU_T in Eq.(9) is minimized under the constraint of the constant value of ΔQ_T^* given by Eq.(10).

By differentiating $m_{A,1}$ in Eq.(10)

$$\partial m_{A,1} / \partial m_{A,n} = \gamma^{-(n-1)} \quad (11)$$

By nullifying the derivatives of Eq.(9) and substituting the above equation

$$\begin{aligned} m_{A,n} &= \sqrt{1+1/\gamma} \gamma^{n/2} m_{A,1} & (2 \leq n \leq N) \\ &= \gamma^{(N+1)/2} m_{A,1} & (n = N + 1) \end{aligned} \quad (12)$$

The value of $m_{A,1}$ is determined by substitution of Eq.(12) into Eq.(10)

$$m_{A,1} = (\Delta Q_T^* / \Delta C_{A,1}) / B \quad (13)$$

in which B is a function of the total number of theoretical stages N and the velocity ratio γ , and is given as

$$B = B(N, \gamma) = 1 + \sqrt{1+1/\gamma} \frac{1 - \gamma^{-(N-1)/2}}{1 - \gamma^{-1/2}} + \gamma^{-(N-1)/2} \quad (14)$$

The most important result shown by Eq.(12) is the fact that the average gradient of isotherm should be increased in the next theoretical stage by a factor of square root of velocity ratio γ .

The total NTU_T for the optimal isotherm determined above is given after some manipulation by substituting Eq.(12) into Eq.(9) as

$$NTU_T = B^2 (\Delta C_{A,1} / \Delta Q_T^*) \quad (15)$$

Similarly the optimal amount adsorbed $Q_{A,n}^*$ is obtained by subtracting cumulatively the

contribution in each stage $m_{A,n} \Delta C_{A,n}$ from the initial value ($Q_{A,0}^*=1$)

$$Q_{A,n}^* = 1 - (1 + \sqrt{1 + 1/\gamma} \frac{1 - \gamma^{-(n-1)/2}}{1 - \gamma^{-1/2}}) \frac{\Delta Q_T}{B} \quad (16)$$

The optimal isotherm can be constructed by plotting the amount adsorbed $Q_{A,n}^*$ given by Eq.(16) against the concentration $C_{A,n}$ given by Eq.(5).

SAMPLE CALCULATION

A sample calculation was carried out for the optimal isotherm and the resultant column height was compared with the case of Langmuir isotherm.

$$q = q_s bc / (1 + bc) \quad (17)$$

The product gas concentration is supposed to decrease to 0.2% of the feed ($C_{A,ex} = 0.002$) under the condition of pressure ratio $\beta = 0.2$ and velocity ratio $\gamma = 1.3$. The best case in a frame of Lagmuir isotherm was sought as a preliminary reference to get the lowest value of the total NTU_T of 28.9 for the parameter of $r (= 1/(1 + bc_{A,in}) = 0.32$.

The total number of theoretical plates is determined as $N = 19$ since $C_{A,n}$ gets lower than the given value of $C_{A,ex}$ ($= 0.002$). The value of ΔQ_T^* is taken as 0.9989 which is identical with the above case of Langmuir isotherm. The total NTU_T is thus obtained to be 27.5 by use of Eq.(15) with the above ΔQ_T^* value, B given by Eq.(14) and $\Delta C_{A,1}$ given by Eq.(6). The value ($= 27.5$) for the optimal isotherm is still lower than the best case ($= 28.9$) of obtained for Freundlich isotherm, too. Thus, the present analysis was found to predict the optimal isotherm which gives the column height shorter than any available isotherms. Axial distributions of concentration, C_A and C_D , and equilibrium amount adsorbed,

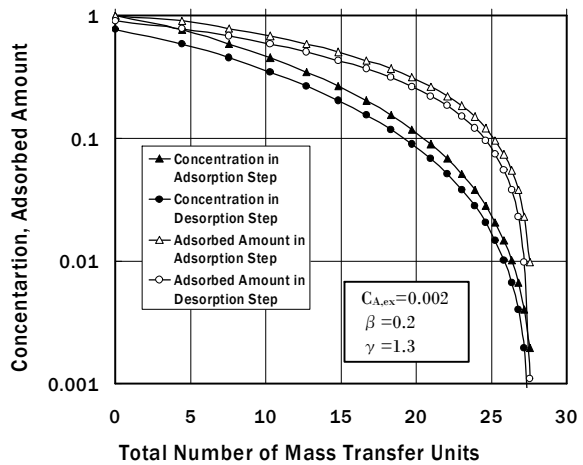


Fig.3 Axial distribution of concentration and equilibrium amount adsorbed .

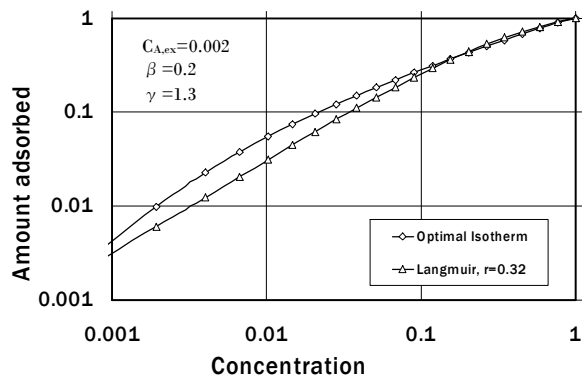


Fig.4 Comparison between the optimum isotherm and Langmuir isotherm with the best parameter

Q^*_A and Q^*_D , are shown in Fig. 3 in terms of NTU instead of direct column height L . In a better design, a sharp change takes place around the product exit end in comparison with a slow change near the feed inlet end so that the driving force $Q^*_A - Q^*_D$ is distributed uniformly through the column.

Adsorption isotherm and concentration profile, respectively, are compared between the present optimal case and the best Langmuir case of $r=0.32$ in Figs. 4 and 5. The amount adsorbed in low concentration region changes sharply in the case of the optimal isotherm as shown in Fig. 4 while it approaches the linear isotherm in Langmuir case. Inversely in middle concentration region, Langmuir isotherm change more rapidly than the optimal. This behavior is reflected in the concentration profile so that the concentration change is greater in low concentration region for the optimal isotherm but in middle concentration region for Langmuir isotherm. The overall effect gives shorter column height for the optimal case ($NTU_T=27.5$) than the Langmuir case ($NTU_T=28.9$).

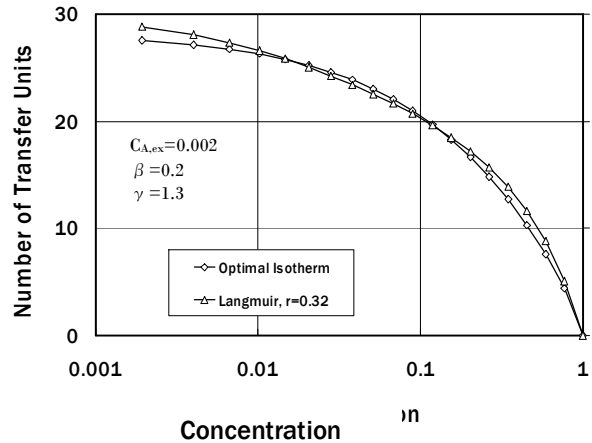


Fig.5 Comparison of concentration distribution between the optimum and Langmuir isotherms

CONCLUSIONS

The fundamental partial differential equations which are inherently time-dependent in PSA were simplified to steady state equations for a short half cycle time or $\lambda = K_{Aat}d / \rho s < 1$. An equilibrium or ideal stage was defined as a section of the column so that the gas streams leaving the section have the same concentration between adsorption and desorption steps. A simple algebraic and graphical method was proposed to evaluate an HETP (height equivalent to a theoretical plate) and the total height of columns. The most "favorable" isotherm to give the shortest column height was constructed by increasing the gradient of isotherm in the next stage by a factor of square root of the velocity ratio. Thus obtained isotherm was better to shorten the column height than any available isotherms even with the best parameters. The validity of this method was confirmed by a sample calculation.

NOMENCLATURE

- a = specific surface area of bed [m^2/m^3]
 b = Langmuir parameter [m^3/mol]
 B = parameter given by Eq.(14) [-]
 c = gas phase concentration under column pressure [mol/m^3]
 $c_{A,in}$ = concentration at feed inlet [mol/m^3]
 $c_{A,ex}$ = concentration at product exit [mol/m^3]
 C = dimensionless concentration relative to $c_{A,in}$ [-]
 K = overall mass transfer coefficient based on solid phase driving force [$\text{kg}/\text{m}^2\text{s}$]
 L_T = total column height [m]
 L_n = HETP (height equivalent to a theoretical plate) of the n-th stage [m]
 m = average gradient of adsorption isotherm, $(\Delta Q/\Delta C)$ [-]
 m_0 = adsorption coefficient for feed concentration $c_{A,in}$ [m^3/kg]
 n = stage number [-]
 N = total number of theoretical plates [-]
 NTU = number of mass transfer units defined by $K_A a m L/u_A$ [-]
 p = pressure in column [Pa]
 q = amount adsorbed [mol/kg]
 $q^*_{A,in}$ = amount adsorbed in equilibrium with feed gas $c_{A,in}$ [mol/kg]
 Q^* = dimensionless amount adsorbed relative to $q^*_{A,in}$ [-]
 r = Langmuir parameter, $1/(1+bc_{A,in})$ [-]
 t_c = half cycle time [s]
 u = superficial gas velocity at column pressure [m/s]
 β = pressure ratio, p_D/p_A [-]
 γ = velocity ratio, u_D/u_A [-]
 κ = Freundlich parameter [-]
 λ = parameter defined by $K_A a t_c/\rho_s$ [-]
 ρ_s = bulk density of bed [kg/m^3]

Subscripts

A, D: adsorption step and desorption step, respectively

in, ex: feed inlet, product exit, respectively

T: total value

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