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Extended Short Cycle Time Analysis of Pressure Swing Adsorption with Nonlinear Adsorption Isotherm

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Abstract. A set of differential equations of material balance for a twin column, two-step PSA (Pressure Swing Adsorption) was expanded into a power series of small value of half cycle time t_c. The effect of finite value of cycle time on the time average product concentration C_{A1} started with the second order term and was interpreted by an additional resistance of mass transfer due to the difference in adsorbed amount between adsorption and desorption steps. Finally the column height L or NTU($N_A = K_A\, amL/u$) required to obtain a given concentration of product gas C_{A1} was given by the following closed form equation for both linear and nonlinear isotherms

$$\left\{\frac{1}{N_A} + \frac{u_A}{u_D}\frac{1}{N_D} + \frac{1}{\nu_\Delta}\right\}^{-1} = \int_{C_{A1}}^{1} \frac{dC_A}{G(C_A) - G(C_D)}, \quad \text{with} \quad C_D = \frac{p_D}{p_A}C_{A1} + \frac{u_D}{u_A}(C_A - C_{A1})$$

in which parameters Ka, L, m, p and u are overall volumetric mass transfer coefficient, column length, adsorption coefficient, pressure and superficial gas velocity, respectively. Subscript A and D refer to adsorption and desorption steps. The function $G(C)$ is a dimensionless adsorption isotherm and the term $1/\nu_\Delta$ is the above mentioned additional mass transfer resistance proportional to square of t_c. The performance prediction by the equation agreed well with more rigorous numerical solutions over a wide range of cycle time by introducing the additional resistance $1/\nu_\Delta$. The concentration swing ΔC_{A1}, i.e. concentration difference during a half cycle time, was also discussed in a frame of the same concept.

Keywords: adsorption, pressure swing adsorption, short cycle time approximation, analytical solution

1. Introduction

Numerical simulation is very often used for the performance prediction of PSA (Pressure Swing Adsorption) widely applied for gas separation and purification. However many variables are coupled complicatedly in a PSA system and hence the performance prediction can not be made straightforwardly even when the system is restricted to a simple case of removal of trace impurities in a twin column, two-step PSA. Then simplified analytical models may reduce complexities of the numerical evaluation. Numerical simulations cannot give any guidance in correlating the effects of variables while analytical solution involves the

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interrelation between variables automatically. The previously proposed "short cycle time analysis" (Hirose and Minoda, 1986; Hirose, 1987) is such an example of analytical solution and was applied successfully to the system operating with relatively short cycle time owing to high amount adsorbed such as in air humidification and CO_2 removal (Lou et al., 2000; Fang et al., 2003). The objective of this study is to obtain a closed analytical form for longer cycle time covering linear and nonlinear adsorption isotherms by extending the short cycle time analysis.

2. Short Cycle Time Approximation

We assume here a single-component adsorption of a dilute adsorbate in a dual column, two-step PSA process. Each column is operated alternately in a high-pressure (adsorption) step and a low-pressure (desorption) step. The basic mass balance is formulated in terms of nondimensional parameters as follows

$$-\frac{\partial C_A}{\partial X} = n_A\frac{\partial Q_A}{\partial \tau} = N_A\{G(C_A) - Q_A\} \qquad (1)$$

$$\frac{\partial C_D}{\partial X} = n_D\frac{\partial Q_D}{\partial \tau} = N_D\{G(C_D) - Q_D\} \qquad (2)$$

where $G(C)$ is an adsorption isotherm in nondimensional form. Then the boundary and cyclic conditions for the periodic steady state lead to

$$C_A = 1 \quad \text{at } X = 0 \qquad (3)$$

$$C_D(\tau) = \beta C_A(\tau - 1) \quad \text{at } X = 1 \qquad (4)$$

$$Q_A = Q_D \quad \text{at } \tau = 1 \qquad (5)$$

$$Q_A(\tau = 0) = Q_D(\tau = 2) \qquad (6)$$

A parameter N_A/n_A $(=K_A a t_c/\rho_s)$ is a ratio of accumulative amount adsorbed during half cycle time relative to the maximum amount adsorbed when complete saturation is attained, and a measure of relative importance of t_c. When the parameter N_A/n_A is a small quantity in a short cycle time operation, a perturbation solution of concentration of product gas C_{A1} expanded around a small value of N_A/n_A can be assumed as follows.

$$C_{A1} = C_{A1}^{(0)} + \frac{N_A}{n_A}C_{A1}^{(1)} + \left(\frac{N_A}{n_A}\right)^2 C_{A1}^{(2)} + \cdots \qquad (7)$$

The zeroth term in Eq. (7) is expressed as an equation below and the first order term equals 0 (Hirose, 1987).

$$\frac{1}{1/N_A + 1/(\gamma N_D)} = \int_{C_{A1}^{(0)}}^{1} \frac{dC_A}{G(C_A) - G(C_D)} \qquad (8)$$

in which concentration in desorption step C_D is given through mass balance as

$$C_D = \beta C_{A1} + \frac{1}{\gamma}(C_A - C_{A1}) \qquad (9)$$

where β is a ratio of the pressure in the desorption step to that in the adsorption step. Similarly, γ is a ratio of superficial velocity. Equation (8) gives a solution of C_{A1} at a limit as half cycle time t_c or N_A/n_A goes to zero.

3. Additional Resistance to Mass Transfer for Linear Isotherm

In the case of linear isotherm, the zeroth and the second order terms in Eq. (7) are given analytically as follows.

$$C_{A1}^{(0)} = \frac{(1 - 1/\gamma)e^{-\nu_1}}{(1 - \beta) + (\beta - 1/\gamma)e^{-\nu_1}} \qquad (10)$$

$$C_{A1}^{(2)} = \frac{1}{12}\left(\frac{C_{A1}^{(0)}\gamma\delta}{1 + \gamma\delta}\right)^2 (1 - \beta)[(1 - e^{-\nu_2}) + \{1/\gamma + \beta(1 - e^{-\nu_2})\}(1 - e^{-\nu_3})] \qquad (11)$$

in which δ is a ratio N_A/N_D. The term ν_1 appearing in Eq. (10) is represented as

$$\nu_1 = \frac{(1 - 1/\gamma)}{1/N_A + 1/(\gamma N_D)} \qquad (12)$$

This denominator is a total mass transfer resistance which is a combination of resistances in the adsorption step and that in the desorption step. On the other hand, the second term of Eq. (7) indicates an effect of performance drop caused by increase of the throughput ratio $1/n_A$ or half cycle time t_c. We here regard this effect as a new additional resistance $1/\nu_\Delta$. Then we add this additional resistance to the total resistance in Eq. (12) and define ν_E as follows.

$$\nu_E = \frac{(1 - 1/\gamma)}{1/N_A + 1/(\gamma N_D) + 1/\nu_\Delta} \qquad (13)$$

Thus the product concentration C_{A1} is assumed to be given by the equation.

$$C_{A1} = \frac{(1 - 1/\gamma)e^{-\nu_E}}{(1-\beta) + (\beta - 1/\gamma)e^{-\nu_E}} \tag{14}$$

in analogy with Eq. (10). After Eq. (14) is expanded into a power series of the unknown parameter $1/\nu_\Delta$, the functional form of $1/\nu_\Delta$ can be determined so that this power series corresponds with Eqs. (10) and (11) within the second power of $1/\nu_\Delta$ as follows.

$$\frac{1}{\nu_\Delta} = \frac{1}{12}\left(\frac{1}{n_A}\right)^2\left(\frac{1+\gamma\delta}{1+\delta}\right)^2(1 + 1/\gamma + \beta) \tag{15}$$

with the small terms $e^{-\nu 2}$ and $e^{-\nu 3}$ neglected. Equation (14) with this term $1/\nu_\Delta$ was found to give a reasonable prediction of C_{A1} over a wide range of $1/n_A$. Note that Eq. (15) was derived for PSA with linear adsorption isotherm.

4. Extended Application of the Additional Resistance $1/\nu_\Delta$ to Nonlinear Adsorption Isotherm

4.1. *Additional Resistance $1/\nu_\Delta$ in Nonlinear Isotherm Cases*

To extend the similar method to nonlinear isotherm cases, we first investigate how the additional resistance $1/\nu_\Delta$ behaves in the case of nonlinear isotherm.

In a similar way to linear isotherm case, we assume the following performance equation by adding a term $1/\nu_\Delta$ to the denominator in left-hand side of Eq. (8).

$$\frac{1}{1/N_A + 1/(\gamma N_D) + 1/\nu_\Delta} = \int_{C_{A1}}^{1} \frac{dC_A}{G(C_A) - G(C_D)} \tag{16}$$

Values of $1/\nu_\Delta$ can be sought by substituting numerical solutions of C_{A1} into Eq. (16) for various sets of parameters. The calculated values of $1/\nu_\Delta$ are plotted against $1/n_A$ in Fig. 1 for the following two isotherms.

$$G(C) = C/\{r + (1-r)C\} \quad \text{(Langmuir type)} \tag{17}$$

$$G(C) = C^{\frac{1}{\kappa}} \quad \text{(Freundlich type)} \tag{18}$$

A line of Eq. (15) for linear isotherm is drawn together to compare the numerical values of $1/\nu_\Delta$ and the dependence on $1/n_A$. Fortunately, there is good agreement in the figure for all values of isotherm parameters. This fact suggests that Eq. (15) originally derived for linear isotherm is effective for PSA with nonlinear isotherms extendedly.

4.2. *Concentration of Product Gas C_{A1}*

We next proceed to compare the numerical solution of C_{A1} with the analytical solution calculated by Eq. (16) using values of $1/\nu_\Delta$ given by Eq. (15) to investigate the validity of the additional resistance. The result of comparison is shown in Figs. 2 and 3 indicating a reasonable agreement between the numerical solution and the analytical solution. As shown in Fig. 1, errors in $1/\nu_\Delta$ become larger as $1/n_A$ goes away from 1.0. But Eq. (15) is effective for wide range of N_A/n_A because the denominator of Eq. (16) is less sensitive to $1/\nu_\Delta$

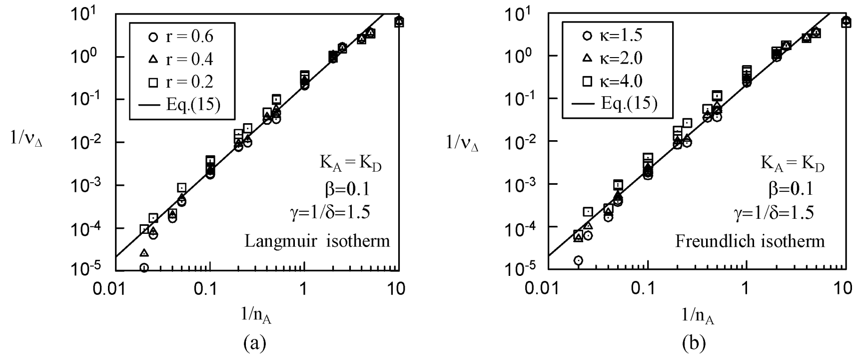
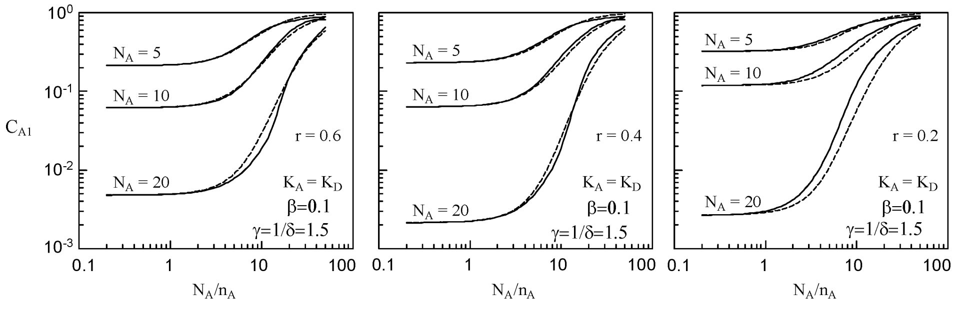
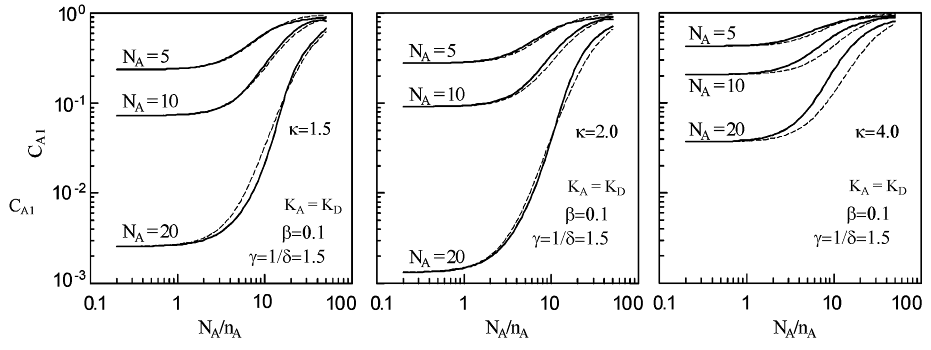


Figure 1. Comparison of numerical values of $1/\nu_\Delta$ with Eq. (15). Isotherm is Langmuir type in (a) and Freundlich type in (b).



(a) (b) (c)

Figure 2. Concentration of product gas C_{A1} in the case of Langmuir isotherm. (a) $r = 0.6$. (b) $r = 0.4$. (c) $r = 0.2$. —— Numerical, - - - - Eq. (16).



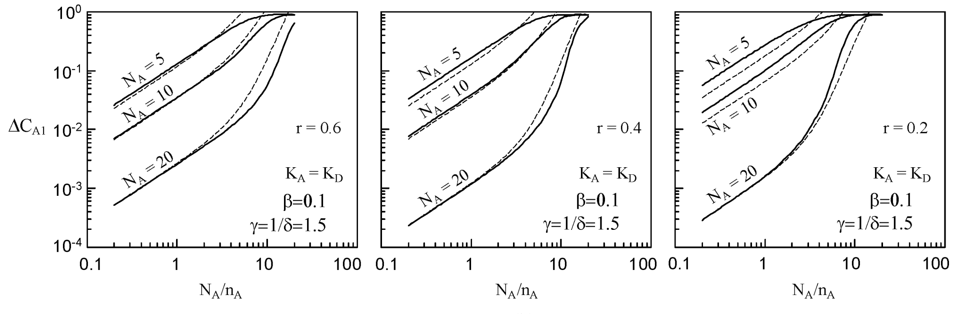
(a) (b) (c)

Figure 3. Concentration of product gas C_{A1} in the case of Freundlich isotherm. (a) $\kappa = 1.5$. (b) $\kappa = 2.0$. (c) $\kappa = 4.0$. —— Numerical, - - - - Eq. (16).

when $1/n_A$ has small values while C_{A1} is less sensitive to $1/\nu_\Delta$ when $1/n_A$ has large values. In Figs. 2 and 3, errors in C_{A1} become larger as isotherm's nonlinearity increases. Nevertheless the errors are less than 50 percent at most, so that rough prediction is possible.

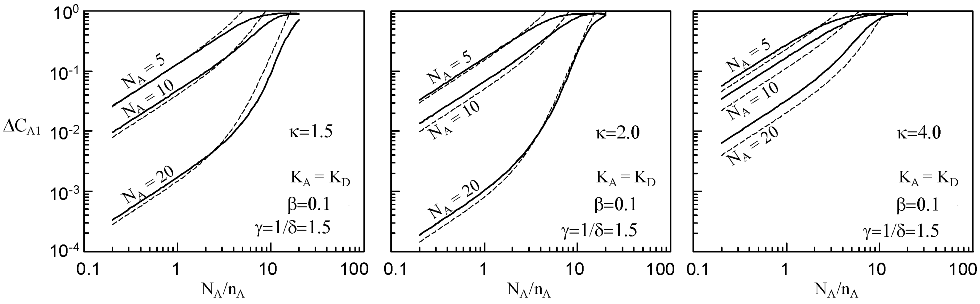
4.3. *Concentration Swing of Product Gas* ΔC_{A1}

The difference between concentration at the beginning of adsorption and that at the end is called concentration swing. The concentration swing is another important



(a) (b) (c)

Figure 4. Concentration swing of product gas ΔC_{A1} in the case of Langmuir isotherm. (a) $r = 0.6$. (b) $r = 0.4$. (c) $r = 0.2$. —— Numerical, - - - - Eq. (19).



(a) (b) (c)

Figure 5. Concentration swing of product gas ΔC_{A1} in the case of Freundlich isotherm. (a) $\kappa = 1.5$. (b) $\kappa = 2.0$. (c) $\kappa = 4.0$. —— Numerical, - - - - Eq. (19).

indicator to characterize the performance of PSA. In case of linear isotherm, concentration swing of product gas ΔC_{A1} approaches asymptotically (Hirose and Minoda, 1986).

$$\Delta C_{A1} = \left(\frac{N_A}{n_A}\right)\frac{1-\beta}{1+\delta}C_{A1} \tag{19}$$

Substituting the values of C_{A1} calculated by Eq. (16) with the $1/\nu_\Delta$ given by Eq. (15) into Eq. (19) gives ΔC_{A1} in the case of nonlinear isotherm. The results are plotted in Figs. 4 and 5. Similarly to the case of concentration of product gas C_{A1}, the dependence on parameters can be expressed by the simple equation Eq. (19) though errors in ΔC_{A1} become larger as isotherm's nonlinearity increases.

5. Conclusions

A design equation for a simple PSA consisting of twin columns and operating with two-steps was investigated on an analytical basis. A concept of additional resistance $1/\nu_\Delta$ originally introduced for PSA with linear adsorption isotherm to apply to a finite value of cycle time is extended successfully to nonlinear isotherm cases. Good agreement in $1/\nu_\Delta$ was confirmed between analytical solution given by Eq. (15) and more rigourous numerical solutions. The PSA performance such as the product concentration C_{A1} given by Eq. (16) and the concentration swing ΔC_{A1} given by Eq. (19) can be evaluated by closed form equations although the errors become larger as isotherm's nonlinearity increases. The analytical solution derived by the short cycle time approximation has the advantage of a closed and structured form even for nonlinear isotherm case.

Nomenclature

a	Specific surface area of bed (m^2/m^3)
C	Dimensionless concentration relative to feed concentration (−)
K	Overall mass transfer coefficient based on solid phase (kg/m^2s)
L	Column length (m)
m	Adsorption coefficient (m^3/kg)
N	Number of mass transfer units defined by $KamL/u$ (−)
$1/n$	Throughput ratio defined by $ut_c/(m\rho_s L)$ (−)
p	Pressure in column (Pa)
Q	Dimensionless amount adsorbed relative to amount adsorbed in equilibrium with feed gas (−)
r	Langmuir parameter in Eq. (17)
t	Time (s)
t_c	Half cycle time (s)
u	Superficial gas velocity at column pressure (m/s)
X	Dimensionless distance from feed inlet relative to column length (−)
β	Pressure ratio, p_D/p_A (−)
γ	Velocity ratio, u_D/u_A (−)
δ	N_D/N_A (−)
κ	Freundlich parameter in Eq. (18)
ν_1	Parameter defined by Eq. (12)
ν_2	$N_A(1+\delta)/(1+\gamma\delta)$
ν_3	$N_A\gamma\delta(1+\delta)/(1+\gamma\delta)$
ρ_s	Bulk density (kg/m^3)
τ	Dimensionless time, t/t_c (−)

Subscripts

0, 1	Feed inlet and product exit
A, D	Adsorption step and desorption step

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