

HYBRID METHOD OF SOLUTION APPLIED TO SIMULATION OF PULSE CHROMATOGRAPHY

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Abstract - In this communication, the method proposed by Cremasco et al. (2003) is applied to predict single and low concentration pulse chromatography. In previous work, a general rate model was presented to describe the breakthrough curve, where a hybrid solution was proposed for the linear adsorption. The liquid phase concentration inside the particle was found analytically and related with the bed liquid phase through Duhamel's Theorem, while the bulk-phase equation was solved by a numerical method. In this paper, this method is applied to describe pulse chromatography of solutes that present linear adsorption isotherms. The simulated results of pulse chromatography are compared with experimental ones for aromatic amino acid experiments from literature.

Keywords: Pulse chromatography; General rate model; Hybrid solution.

INTRODUCTION

The association of chromatographic technique and moment analysis of the response peaks is a powerful approach for adsorption studies. The moment analysis in chromatography and, as extension, the pulse analysis have been applied to measure the transport rate, adsorption parameters and bed characteristics for single component (Yamamoto et al., 2001; Harlick and Tezel, 2000, 2003; da Silva et al., 2005) or multicomponent (Chihara et al, 2005) systems. This method was applied to porous solids, such as the adsorption of sulfur dioxide on 13X molecular sieve and activated carbon, and to evaluate effective diffusion coefficients in a macroreticular resin catalyst (Dogan and Dogu, 2003). The pulse chromatographic method can be used to evaluate the influence of packing (Wu and Ching, 2002), and connecting devices, such as frits, on the performance of a chromatographic column (Wu and Ching, 2003). The behavior of a

chromatographic column where a single solute is fed in the presence of a suitable modifier can be analyzed in the context of the pulse propagation of the solute, whose retention depends on the modifier concentration, as studied by Ströhlein et al. (2006), who analyzed the phenomenon as a full-fledged binary problem.

In this paper, the method proposed by Cremasco et al. (2003) is applied to predict single and low concentration pulse chromatography. A general rate (GR) model is presented, and a hybrid method is used. Solid-phase concentration is found by analytical solution, and it is correlated with liquid-bed concentration through Duhamel's theorem (Rosen, 1952), while solution of the moving-phase equation is obtained by a numerical method.

THEORY

The modeling strategy chosen to represent the pulse chromatographic process consists of a dynamic

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modeling of an adsorption column, which is modeled by a general rate model. In order to obtain this mathematical model, some assumptions are fixed: the flow rate is constant; the transversal cross section is constant for and through the column; radial dispersion is negligible; the axial dispersion coefficient is a function of solute and flow rate; the external mass transfer resistance is considered; the solids are made of spherical particles with uniform radius; the solution is dilute and thus adsorption isotherm is linear; and the

pore diffusion model describes the intra-particle transport mechanism. These assumptions were applied to the description of the breakthrough curve (Cremasco et al, 2003), the model of which is summarized in Table 1. In the condition (8), C_{in} is the solute concentration in the flow entering the column. In the present work, the mathematical modification from breakthrough curve to pulse curve lies in the choice of C_{in} . This concentration is not constant, but it is where the pulse condition appears.

Table 1: General rate model for linear adsorption (Cremasco et al., 2003).

Solid Phase	$\left[\varepsilon_p + (1 - \varepsilon_p)k_p \right] \frac{\partial C_p}{\partial t} = \varepsilon_p D_p \left(\frac{2}{r} \frac{\partial C_p}{\partial r} + \frac{\partial^2 C_p}{\partial r^2} \right) \quad (1)$ $C_p = 0 \quad \text{for } t = 0 \quad (2)$ $\frac{\partial C_p}{\partial r} = 0 \quad \text{for } r = 0 \quad (3)$ $\frac{\partial C_p}{\partial r} = \frac{k_f}{\varepsilon_p D_p} (C - C_p) \quad \text{for } r = R \quad (4)$	<p>C_p, solute concentration in the liquid phase inside the particle pores (volume fraction ε_p); R, particle average radius; k_f, external mass transfer coefficient from (Wilson and Geankopolis, 1966)</p> $k_f = \frac{0.545 \cdot D_{AB} \cdot Pe_{MP}^{1/3}}{R \cdot \varepsilon}; \quad \text{with } Pe_{MP} = \frac{2uR\varepsilon_p}{D_{AB}}$ <p>D_{AB}, free diffusion coefficient; and D_p is effective diffusion coefficient (Mackie and Meares, 1955):</p> $D_p = \frac{\varepsilon_p}{(2 - \varepsilon_p)^2} D_{AB}$
Fluid Phase	$\frac{\partial C}{\partial t} = E_b \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - \frac{1 - \varepsilon}{\varepsilon} Ra \quad (5)$ $Ra = \frac{3}{R^3} \left[\varepsilon_p + (1 - \varepsilon_p)k_p \right] \frac{\partial}{\partial t} \left\{ \int_0^R C_p r^2 dr \right\} \quad (6)$ $C = 0 \quad \text{for } t = 0 \quad (7)$ $\frac{\partial C}{\partial z} = 0 \quad \text{for } z = L_c \quad (8)$ $\frac{\partial C}{\partial z} = \frac{u}{E_b} (C - C_{in}) \quad \text{for } z = 0 \quad (9)$	<p>C is the solute concentration in the fluid phase (volume fraction ε); u, interstitial velocity; Ra is the rate of adsorption/desorption of solute by the solid, by reactor volume unit; k_p, equilibrium partition constant; L_c is effective column length; E_b is the axial dispersion coefficient (Athayle et al., 1992):</p> $\frac{E_b}{uR} = 2 \left(\frac{Pe_{MP}}{1 - \varepsilon} \right)^{1/6}$

$$C_{in} = C_0 \quad \text{for } 0 \leq t < t_0 \quad (10)$$

$$C_{in} = 0 \quad \text{for } t_0 < t \quad (11)$$

The resolution method employed is a hybrid method, based on previous work which was developed for prediction of breakthrough curves for the adsorption of a single compound. The intra-particle liquid solute concentration is found analytically and correlated to the liquid bed concentration through Duhamel's theorem. The use of this theorem results in an equation connecting the intraparticle liquid concentration, C_p , to the liquid bed concentration, C . This method is described in Cremasco et al. (2003).

RESULTS AND DISCUSSION

Numerical results are obtained for two amino acids, phenylalanine (Phe) and tyrosine (Tyr). The solute properties (D_{AB} and k_p) presented in Table 2, and the physical parameters of the column, Table 3, are found in the literature (Cremasco et al., 2001). The axial dispersion coefficient, E_b , and the external mass transfer coefficient, k_f , are derived from the literature (Table 1).

Table 2: Solute properties (Cremasco et al., 2001)

Solute	k_p	D_p (cm ² /min)
Phe	1.947	1.02×10^{-4}
Tyr	3.229	1.01×10^{-4}

Table 3: Column and adsorbent properties (Cremasco et al., 2001)

L_c (cm)	D (cm)	ϵ	R (μ m)	ϵ_p
12.5	1.5	0.37	180	0.55

The simulated curves are compared with experimental ones of Tyr and Phe, obtained by Cremasco et al. (2001), in Figures 1 and 2, respectively. In both cases, two different flow rates were investigated: 1,0 ml/min (Q1) and 2,5 ml/min (Q2).

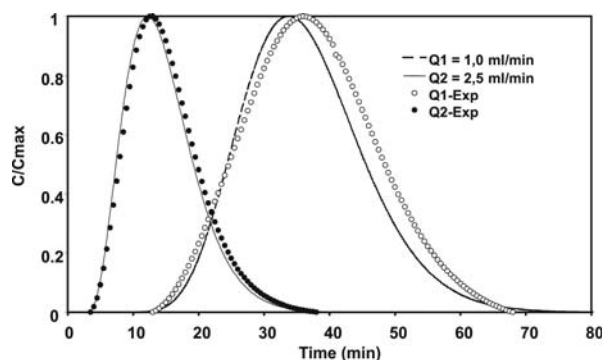


Figure 1: Comparison between theoretical and experimental results for tyrosine Tyr.

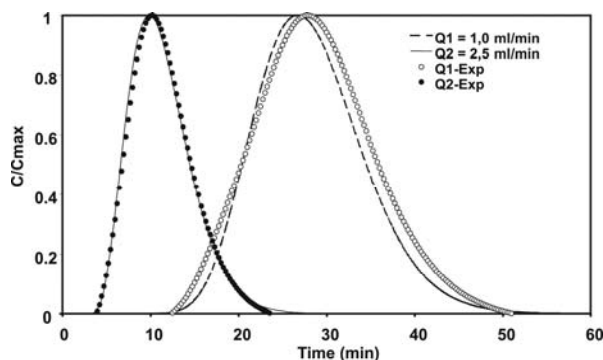


Figure 2: Comparison between theoretical and experimental results for phenylalanine Phe

As can be seen, model predictions are in close agreement with experimental results. This tends to show that the method applied is suitable for prediction, since the model parameters were not adjusted. A small discrepancy appears at low flow rate. In this case, the axial dispersion estimate from the Athayle et al. (1992) correlation, Table 1, is under estimated due to effects of dispersion off column, such as the presence of the loop.

This method proved to be easier and less computer demanding than the purely analytical methodology. In this case, several mathematical models were developed, with analytical solution for linear isotherm (Ruthven, 1984; Carta, 1988). However, these analytical solutions are expressed in infinite integral form, which is necessary to solve by a numerical method, which is particularly difficult because of the oscillating behavior of the integrand (Rasmuson, 1981, 1985). Simplified models, such as transport-dispersive or equilibrium-dispersive, can be adjusted to experimental data. It has been shown that a general rate model (GR) should be preferred for prediction, since their coefficients do not need to be adjusted with experimental results (Guiochon, 2002). In the present work, these coefficients were predicted by correlations from literature, as showed at Table 1.

CONCLUSIONS

A hybrid method for the numerical simulation of pulse chromatography is presented in this paper and the results are compared with experimental data from the literature. It is shown that the numerical method developed offers satisfactory predictive results in a short time in comparison to the physical separation process. Still, discrepancies between theoretical and experimental curves appear due to

axial dispersion deviation at lower flow rate. On the other hand, this work shows that the numerical scheme developed is efficient and offers fast, reliable results using a general rate model. The main limitation of this approach is the fact that Duhamel's theorem is only applicable to linear PDE with linear initial and boundary conditions. However, the same limitation holds for the entirely analytical solution, since it is based on the same model (Rosen, 1952). The analytical solution has the disadvantage that it is quite difficult to calculate, since it is expressed as an integral of an oscillatory function that is very difficult to compute numerically. The hybrid approach used here avoids this difficulty. On the other hand, the results indicated that the method was efficient and easy to apply, solving the problem in a very short computational time.

REFERENCES

- Athalye, A. M., Gibbs, S. J., and Lightfoot, E. N., Predictability of Chromatographic Protein Separations: Study of Size-exclusion Media with Narrow Particle Size Distribution, *J. Chrom.*, 589, p. 71 (1992).
- Carta, G., Exact Analytic Solution of a Mathematical Model for Chromatographic Operations, *Chem. Eng. Sci.*, 43 (10), p. 2877 (1988).
- Dogan, M., Dogu, G. Dynamics of Flow and Diffusion of Adsorbing Gases in Al_2O_3 and $\text{Pd-Al}_2\text{O}_3$ Pellets. *AIChE Journal*, 49 (12), p. 3188 (2003).
- Chihara, K., Kaneko, Y., Terakado, T., Mizuochi, H. Study of Multicomponent Gas Adsorption into MSC5A by Chromatograph. *Adsorption*, 11, p. 249 (2005).
- Cremasco, M. A., Hritzko, B. J., Xie, Y. and Wang, N.-H.L., Parameters Estimation for Amino Acids Adsorption in a Fixed Bed by Moment Analysis, *Brazilian J. Chem. Eng.*, 18, (2), p.181, (2001).
- Cremasco, M. A., Guirardello, R. and Wang, N. -H. L., Adsorption of Aromatic Amino Acids in a Fixed Bed Column, *Brazilian J. Chem. Eng.*, 20, (3), p. 327,(2003).
- Da Silva Jr., I., J., Veredas, V., Carpes, M. J. S., Santana, C, C., Chromatographic Separation of Bupivacaine Enantiomers by HPLC: Parameters Estimation of Equilibrium and Mass Transfer Under Linear Conditions. *Adsorption* 11, p. 123 (2005).
- Harlick, P. J. E., Tezel, F. H., A Novel Solution Method for Interpreting Binary Adsorption Isotherms from Concentration Pulse Chromatography Data. *Adsorption* 6, p. 293 (2000).
- Harlick, P. J. E., Tezel, F. H., Use of Concentration Pulse Chromatography for Determining Binary Isotherms: Comparison with Statically Determined Binary Isotherms. *Adsorption* 9, p. 275 (2003).
- Guiochon, G., Preparative Liquid Chromatography: Review, *J. of Chrom. A*, 965, p.129 (2002).
- Mackie, J. S., and Meares, P., The Diffusion of Electrolytes in a Cation-exchange Resin Membrane, *Proc. Roy. Soc. London, Seria A*, 232, p. 498, (1955).
- Rasmuson, A., Exact Solution of a Model for Diffusion and Transient Adsorption in Particle and Longitudinal Dispersion in Packed Beds, *AIChE*, 27 (6), p. 1032 (1981).
- Rasmuson, A., Exact Solution of a Model for Diffusion in Particles and Longitudinal Dispersion in Packed Beds: Numerical evaluation, *AIChE*, 31, (3), p. 518 (1985).
- Rosen, J. B., Kinetics of a Fixed Bed System for Solid Diffusion into Spherical Particle, *J. Chem. Phys.*, 20, (3), p. 387 (1952).
- Rutheven, D. M., Principles of Adsorption and Adsorption Process, Wiley-Interscience, New-York (1984).
- Ströhlein, G., Morbidelli, M., Rhee, H-K., Mazzotti, Modeling of Modifier-Solute Peak Interactions in Chromatography *AIChE Journal*, 52 (2), p. 565 (2006).
- Yamamoto, S., Akio Okamoto, A., Watler, P., Effects of Adsorbent Properties on Zone Spreading in Expanded Bed Chromatography. *Bioseparation* 10, p. 1 (2001).
- Wilson, E. J., and Geankopolis, C. J., Liquid Mass Transfer at Very Low Reynolds Numbers in Packed Beds, *Ind. Eng. Chem. Fundam.*, 5, p. 9 (1966).
- Wu, Y, X. C. B., Ching, C. B., The Theoretical Study of the Effect of Packing Heterogeneity on HPLC by Computational Fluid Dynamics. *Chromatographia* 56 (11/12), p. 679 (2002).
- Wu, Y. X. C. B., Ching, C. B., Theoretical Study of the Effect of Frit Quality on Chromatography Using Computational Fluid Dynamics. *Chromatographia* 57 (5/6), p. 239 (2003).