



Analysis of linear two-dimensional general rate model for chromatographic columns of cylindrical geometry



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ABSTRACT

This work is concerned with the analytical solutions and moment analysis of a linear two-dimensional general rate model (2D-GRM) describing the transport of a solute through a chromatographic column of cylindrical geometry. Analytical solutions are derived through successive implementation of finite Hankel and Laplace transformations for two different sets of boundary conditions. The process is further analyzed by deriving analytical temporal moments from the Laplace domain solutions. Radial gradients are typically neglected in liquid chromatography studies which are particularly important in the case of non-perfect injections. Several test problems of single-solute transport are considered. The derived analytical results are validated against the numerical solutions of a high resolution finite volume scheme. The derived analytical results can play an important role in further development of liquid chromatography.

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1. Introduction

Mathematical modeling of liquid chromatography has been an attractive field of research since the 1960s, leading to a more efficient use of chromatographic columns. The approach provides important information about physical and thermodynamical kinetics as well as flow phenomena through packed-beds. Understanding of the effects of operating variables and parameters characterizing the column is needed for an accurate theoretical analysis of the elution profiles and to optimize the operating conditions [1–3]. Different mathematical models exist in the literature describing the chromatographic process. The most notable amongst them are the general rate model (GRM), the equilibrium dispersive model (EDM) and the lumped kinetic model (LKM) [1–9]. All these models need important input information regarding the thermodynamic equilibrium of the distribution of the components between the mobile and stationary phases. They differ essentially regarding the consideration of unavoidable mass transfer processes, which cause undesired band broadening [1,2].

In the literature, analytical solutions for one-, two- and three-dimensional advection-dispersion equations (ADEs) have been

developed for predicting the transport of various contaminants in the soil. The analytical solutions of the one-dimensional ADE subject to various initial and boundary conditions were derived in [10]. The analytical solutions of the two-dimensional ADE with various source boundary conditions were presented in [11,12]. The analytical solutions for three-dimensional ADE were derived in [13,14]. However, these models were mostly limited to ADE in Cartesian coordinates describing steady uniform flow [14]. The analytical solutions of the two-dimensional ADE in cylindrical coordinates are particularly useful for analyzing problems of the two-dimensional solute transport in a porous medium system with steady uniform flow [14–19].

In the liquid chromatography, the analytical solutions and moment analysis of the one-dimensional EDM, LKM and GRM have been derived for linear isotherms using the Laplace transformation [4–9,20,21]. Very recently, we have derived analytical solutions and temporal moments of linear 2D-EDM and 2D-LKM for simulating liquid chromatography in cylindrical columns [22–24]. This article extends those analysis to linear 2D-GRM.

Moment analysis is a useful and effective technique for deducing important information about the retention equilibrium and mass transfer kinetics in a fixed-bed column. The moment generating property of the Laplace domain solutions can be used to derive analytical temporal moments. These moments can be used to get important information about the retention

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times, band broadenings, and front asymmetries. Several authors have derived moments for various boundary conditions (BCs) [5–8,20,21,2,25–37].

In this article, the above analysis is further extended by analytically solving a 2D-GRM through simultaneous implementation of Hankel and Laplace transformations. In the current scenario, no analytical Laplace inversion is possible. Therefore, numerical Laplace inversion is applied to get back semi-analytical solutions in the actual time domain [38]. To analyze the effects of different kinetic parameters, statistical temporal moments are derived from the Hankel and Laplace transformed solutions. A high resolution upwind finite-volume scheme (HR-FVS) is extended to numerically approximate the current model equations [39,40]. To illustrate the potential of the current analysis, several case studies are carried out considering a wide range of mass transfer kinetics. Also, relations are derived for matching the first two moments of 2D-GRM and simplified 2D-LKM. The derived semi-analytical results are critically checked against the numerical solutions of the suggested HR-FVS.

The novelty of this article specifically include: (a) the derivation of analytical solutions of linear 2D-GRM for two different sets of boundary conditions, (b) injection of specific profiles to amplify the effect of possible rate limitations of the mass transfer in the radial direction, (c) derivation of useful moment expressions, (d) implementation of a numerical scheme to the model equations, and (e) derivation of relations among the kinetic parameters of 2D-GRM and 2D-LKM through comparison of their respective moments. The derived analytical and numerical solutions are useful tools for further developments in the liquid chromatography. For instance, this analysis can be used to study the effects of mass transfer kinetics on the elution profiles, for sensitivity analysis, for validating numerical solutions, and for determining longitudinal and radial dispersion coefficients from experimentally determined elution profiles, among others. The studied 2D-model is more general and flexible than the classical 1D-models [7].

The current 2D-model can be useful if (i) the injection at the column inlet is not perfect (i.e. a radial profile is introduced at the column inlet), (ii) the column is not homogeneously packed (which is more probable for larger columns), (iii) there are radial temperature gradients, which are connected also with radial concentration gradients. All such scenarios can happen in reality. In many chromatography processes, deviations from predictions using a simpler 1D model might be small. However, the differences are difficult to evaluate and it is desirable to have quantitative tools and criteria to rationally select the right model. With our current 2D-GRM model, we can study the situation (i) by assuming injections in inner cylindrical core or outer annular region. Situations (ii) and (iii) are more complicated and require further model extensions, for example we have to consider variable column porosities and to include energy balance equation in the current model equations. Such extensions require more detailed treatment which is outside the scope of this paper.

The remaining parts of this article are organized as follows. In Section 2, the linear 2D-GRM model is introduced. In Section 3, the analytical solution of 2D-GRM for considered two types of boundary conditions are derived. In Section 4, analytical temporal moments are derived. In Section 5, the numerical test problems are presented. Lastly, concluding remarks are given in Section 6.

2. The mathematical model of 2D-GRM

In liquid chromatography, the 2D-GRM considers several contributions of the mass transfer processes that lead to band broadening. Let t denotes the time coordinate, z represents the axial coordinate along the column length and ρ be the radial coordinate along the

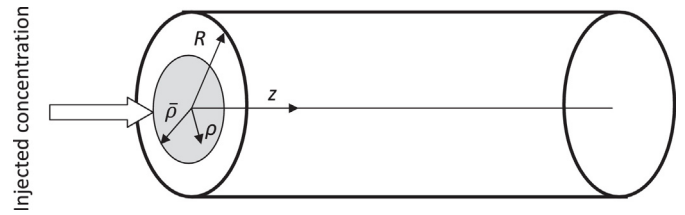


Fig. 1. Schematic diagram of a cylindrical chromatographic column packed with uniform spherical particles.

column radius. The solute travels along the column axis in the z -direction by advection and axial dispersion and spreads along the column radius in the ρ -direction by radial dispersion. The following particular injection conditions are assumed to amplify the effects of mass transfer in the radial direction. The inlet cross section of the column is divided into an inner cylindrical core and an outer annular ring (see Fig. 1) by introducing a new parameter $\bar{\rho}$. The injection can be done either through an inner core, an outer ring or through the whole cross section. The latter case results if $\bar{\rho}$ is set equal to the radius of the column denoted by R . Since in the latter case no initial radial gradients are provided, the solutions should converge into the solution of the simpler one-dimensional model [7]. It is, however, important to mention that probably the practical relevance of such kind of injections is of minor importance.

The mass balance equation for a single-solute percolating through a cylindrical column of radius R filled with spherical particles of radius R_p is given as

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial z} = D_z \frac{\partial^2 c}{\partial z^2} + D_\rho \left(\frac{\partial^2 c}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial c}{\partial \rho} \right) - \frac{3}{R_p} F k_{\text{ext}} (c - c_p(r_p = R_p)). \quad (1)$$

In the above equation, c is the concentration of a solute in the bulk phase of the fluid, c_p is the concentration of the solute in the pores of the particles, u is the interstitial velocity, D_z is the axial dispersion coefficient, and F is the phase ratio which is defined in term of the external porosity ϵ_b as $F = (1 - \epsilon_b)/\epsilon_b$. Moreover, D_ρ represents the radial dispersion coefficient, k_{ext} is the external mass transfer coefficient and r_p is the radial coordinate of spherical particles.

The mass balance equation in the pores of the particles, considering two mechanisms of intraparticle transport, can be expressed as

$$\epsilon_p \frac{\partial c_p}{\partial t} + (1 - \epsilon_p) \frac{\partial q_p^*}{\partial t} = \frac{1}{r_p^2} \frac{\partial}{\partial r} \left[r_p^2 \left(\epsilon_p D_p \frac{\partial c_p}{\partial r_p} + (1 - \epsilon_p) D_s \frac{\partial q_p^*}{\partial r_p} \right) \right], \quad (2)$$

where, q_p^* is local equilibrium concentration of the solute in the stationary phase, D_p is the pore diffusivity, ϵ_p is the internal porosity, and D_s is the surface diffusivity. In the current case of diluted systems, the following linear isotherm is used:

$$q_p^* = a c_p. \quad (3)$$

In the above equation, a denotes the Henry's coefficient. In order to simplify the notations and reduce the number of variables, the following dimensionless variables are introduced:

$$C = \frac{c}{c_{\text{inj}}}, \quad C_p = \frac{c_p}{c_{\text{inj}}}, \quad \tau = \frac{ut}{L}, \quad x = \frac{z}{L}, \quad \psi = \frac{\rho}{R}, \quad r = \frac{r_p}{R_p},$$

$$Pe_z = \frac{Lu}{D_z}, \quad Pe_\rho = \frac{R^2 u}{D_\rho L}, \quad Bi = \frac{k_{\text{ext}} R_p}{D_{\text{eff}a}}, \quad \eta = \frac{D_{\text{eff}} L}{u R_p^2},$$

$$\xi = 3 Bi \eta F = \frac{3 L F k_{\text{ext}}}{u R_p}. \quad (4)$$

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