Two-dimensional non-equilibrium model of liquid chromatography: Analytical solutions and moment analysis

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HIGHLIGHTS

- An analysis of two-dimensional (2D) LKM for liquid chromatography is presented.
- The developed analytical solutions extended the solutions for 2D-EDM.
- The finite Hankel and Laplace transforms are jointly applied to solve the model.
- The solutions quantify the influence of solute transport in radial direction.
- For further analyses, temporal moments are derived.

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ABSTRACT

This paper presents a set of semi-analytical solutions and analytical moments for two-dimensional lumped kinetic model (LKM) describing non-equilibrium solute transport through a chromatographic column of cylindrical geometry. General solutions are derived for the solute concentration by successive implementation of finite Hankel and Laplace transforms assuming different sets of boundary conditions and linear sorption kinetic process. For further analysis, statistical temporal moments are derived from the Laplace transformed solutions. The current solutions extend and generalize the recent solutions of two-dimensional equilibrium dispersive transport model (EDM). Typical examples of concentration profiles and moments resulting from different sets of initial and inlet conditions are presented and briefly discussed. The derived semi-analytical solutions for concentration profiles and analytical moments are validated against the numerical results of a high resolution finite volume scheme. Good agreements in the results verify the correctness of analytical solutions and accuracy of the proposed numerical algorithm.

1. Introduction

The influence of axial and radial mass transfer kinetics in a cylindrical chromatographic column on the elution profile of a pulse of a mixture and on the degree of resolution achieved between the bands of different components is a fundamental problem in preparative chromatography. Chromatographic processes provide a powerful tool for the separation of multicomponent mixtures in which the components have different adsorption affinities, especially when the components show separation factors near one and high resolutions, yields and purities are required. Typical applications are found in the pharmaceutical and food industries where standard thermal unit operations like distillation are not suitable. Chromatography technology has received considerable attention during the last few decades. More advances have been made in this process by frequently improving their performances for the separation of more composite mixtures, see Guiochon (2002), Guiochon and Lin (2003), Guiochon et al. (2006), and Ruthven (1984).

Mathematical modeling is an essential part of the chromatographic theory for describing its dynamical process. It provides a procedure for predicting the dynamical behavior of solute in the column without extensive experiments. Due to different considerations of simplifications, several types of models have been established and applied to illustrate the behavior of chromatographic columns. These include the general rate models, the lumped kinetic model, the linear driving force models, the linear models, and the equilibrium dispersive models, see e.g. Carta (1988), Guiochon

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(2002), Guiochon and Lin (2003), Guiochon et al. (2006) and Ruthven (1984). All these models need an important input information regarding the thermodynamic equilibrium of the distribution of the components between the mobile and stationary phases. These models are categorized as non-equilibrium and equilibrium transport models. In the equilibrium models sorption is presumed to be instantaneous, while sorption in the non-equilibrium models is thought to be governed by first-order kinetics, see Guiochon (2002), Guiochon et al. (2006), and Ruthven (1984). Generally, only the most relevant concentration gradients occurring along the column axis are considered within the one-dimensional (1D) models. Gradients along the radial coordinate of the columns requiring the solution of two-dimensional (2D) models are typically neglected.

A number of analytical solutions for one-, two- and three-dimensional advection–dispersion equations (ADEs) have been developed for predicting the transport of various contaminants in the subsurface. For example van Genuchten and Alves (1982) formulated several analytical solutions of the one-dimensional ADE subject to various initial and boundary conditions. Batu (1989, 1993) and Coimbra et al. (2003) presented analytical solutions of the two-dimensional ADE with various source boundary conditions. Leij et al. (1991) and Park and Zhan (2001) derived analytical solutions for three-dimensional ADE. However, these models were mostly limited to ADEs in Cartesian coordinates with steady uniform flow, see e.g. Park and Zhan (2001). Analytical solutions for two-dimensional ADEs in cylindrical coordinates are particularly useful for analyzing problems of the two-dimensional solute transport in a porous medium system with steady uniform flow, see for example Chen et al. (2011a,b), Massabò et al. (2011), Massabó et al. (2006), Park and Zhan (2001), and Zhang et al. (2006).

Analytical solutions of the models for column chromatography are possible when mass transfer processes are represented by linear relationships, see e.g. Carta (1988), Guiochon et al. (2006), Javeed et al. (2013), Li et al. (2003a,b), Li et al. (2011), and Qamar et al. (2013). Although with the increased computational power of digital computers and with the availability of accurate of numerical algorithms, analytical solutions have lost some of their importance, they still generally present the very significant advantage of providing greater insight into the operation of the process and can be more easily implemented as a routine design tool. These solutions help tremendously to understand and analyze, without extensive experiments, the dynamics of concentration fronts moving through chromatographic columns. The availability of such solutions further provides useful tools to determine free transport parameters of the corresponding models. Finally, the solutions are most helpful for the validation of numerical methods needed to solve more general cases.

Moment analysis is known to be an effective method for deducing important information about the retention equilibrium and mass transfer kinetics in a chromatographic column. Provided analytical solutions of the column mass balances are available, condensed information in the form of moments of the outlet profiles can be easily obtained. Moment analysis has been comprehensively discussed in the literature, see for instance Antos et al. (2003), Guiochon et al. (2006), Kubin (1965a,b), Kucera (1965), Lenhoff (1987), Miyabe and Guiochon (2000, 2003), Miyabe (2007, 2009), Ruthven (1984), Schneider and Smith (1968), Suzuki (1973), and Wolff et al. (1980a,b). Recently, Javeed et al. (2013) and Qamar et al. (2013, 2014) used the Laplace transformation to derive analytical solutions of one-dimensional EDM, LKM and GRM models. Moreover, the authors also derived the moments of Laplace transformed solutions for different sets of boundary conditions (BCs).

This manuscript extends and generalizes our recent solutions for two-dimensional EDM to the solutions of two-dimensional LKM describing non-equilibrium solute transport through a chromatographic column of cylindrical geometry, see Qamar et al. (2014). General solutions are derived for the solute concentration by applying finite Hankel transform together with Laplace transform, see e.g. Carslaw and Jaeger (1953); Crank (1975), Chen et al. (2011a,b), and Qamar et al. (2014). The finite Hankel transform technique is utilized to eliminate the radial coordinate, followed by the application of the Laplace transform to solve the resulting partial differential equations assuming both Dirichlet and Robin (Danckwerts) inlet boundary conditions (BCs) and linear sorption kinetic process. For further analysis, statistical temporal moments are derived from the Laplace transformed solutions, see e.g. Qamar et al. (2013, 2014). Typical examples of concentration profiles and moments resulting from different sets of initial and inlet conditions are presented and briefly discussed. The derived semi-analytical solutions for concentration profiles and analytical temporal moments are validated against the numerical results of a high resolution finite volume scheme, see Javeed et al. (2011). Good agreements in the results verify the correctness of analytical solutions and accuracy of the proposed numerical algorithm.

2. Mathematical model

The chromatographic process involves complex hydrodynamic, thermodynamic, and kinetic phenomena, which often interact. In the simple EDM only one parameter is used to describe band broadening phenomena. In reality, many influential contributions take place simultaneously during migration of the solute. It is often impossible to identify one single contribution as rate determining. The LKM incorporates the rate of variation of the local concentration of solute in the stationary phase and back-mixing in the column due to dispersion. The model lumps hereby the contribution of internal and external mass transport resistances into a mass transfer coefficient denoted by k.

This study considers the non-equilibrium transport of a solute in a two-dimensional chromatographic column of radial geometry as illustrated schematically in Fig. 1. The injected solute migrates in the z-direction by advection and axial dispersion, whereas it spreads in the r-direction by radial dispersion. We consider the flow rate variation of the local solute concentration and it is assumed that the adsorption isotherm is linear with a Henry constant a. To trigger and amplify the effect of possible rate limitations of the mass transfer in the radial direction, the following specific injection conditions are assumed. By introducing a parameter $\tilde{r}$ the inlet cross section of the column is divided into an inner cylindrical core and an outer annular ring (see Fig. 1). The injection profile is formulated in a general way allowing for injection either through an inner core, an outer ring or through the whole cross section. The latter case results if $\tilde{r}$ 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, see Javeed et al. (2013).

Based on the above setup, the governing equations of a two-dimensional linear LKM for a fixed bed chromatography column
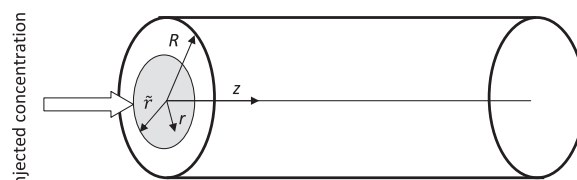

Fig. 1. Schematic representation of a chromatographic column of cylindrical geometry. It is assumed that solute can be injected either through inner cylindrical core or through outer annular ring.