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Analytical and numerical solutions of two-dimensional general rate models for liquid chromatographic columns packed with core–shell particles

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This work is concerned with the analytical and numerical solutions of linear and nonlinear two-dimensional general rate models (2D-GRMs) describing the transport of single-solute and multi-component mixtures through chromatographic columns of cylindrical geometry packed with core–shell particles. The finite Hankel and Laplace transformations are successively applied to derive analytical solutions for a single-solute model considering linear adsorption isotherms and two different sets of boundary conditions. Moreover, analytical temporal moments are derived from the Laplace domain solutions. The process is further analyzed by numerically approximating the nonlinear 2D-GRM for core–shell particles considering multi-component mixtures and nonlinear Langmuir isotherm. A high resolution finite volume scheme is extended to solve the considered 2D-model equations. Several case studies of single-solute and multi-component mixtures are considered. The derived analytical results are validated against the numerical solutions of a high resolution finite volume scheme. Typical performance criteria are utilized to analyze the performance of the chromatographic process. The results obtained are considered to be useful to support further development of liquid chromatography.

1. Introduction

Chromatography exploits specific interactions of the components present in the mixtures to be separated with dedicated solid stationary phases. Numerous types of particles have been developed and are applied successfully (Kirkland et al., 2000; Fekete et al., 2010; Rissler, 2000; Xiang et al., 2003; Miyabe, 2008; Manchon et al., 2010; Wang et al., 2007; Gu et al., 2011). Nonporous particles have been found successful in analytical liquid chromatography because they provide fast separation times (Fekete et al., 2010; Rissler, 2000; Xiang et al., 2003). The widely applied fully porous particles cause intraparticle mass transfer limitations reducing the column efficiencies. The use of core–shell particles (or superficially porous Kirkland et al., 2000 or fused-core Manchon et al., 2010 or cored beads Wang et al., 2007) can provide optimum conditions by avoiding the shortcomings of fully porous and nonporous particles. Fully porous particles can offer the large binding capacities with only moderate intraparticle

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mass transfer resistances (Gu et al., 2011). The use of core–shell particles has generated recently considerable interests in both analytical and preparative liquid chromatography (Ning et al., 1998; Schuster et al., 2010; Zhou et al., 2004). They have been used for example, for the separation of peptides and other compounds (Kiss et al., 2010; Ning et al., 1998), nucleotides (Kirkland et al., 2000), and proteins (Zhou et al., 2007). Moreover, several theoretical investigations have been carried out on the use of core–shell particles by considering one-dimensional (1D) chromatographic models. Kaczmarski and Guiochon (2007) used the general rate model to study fully porous particles and the lumped particle model to study thin-shelled coated beads. Li et al. (2010) carried out optimization of core size for linear chromatography by minimizing HETP numbers. Miyabe (2008) showed that a column packed with cored beads can achieve higher resolution as compared to a column packed with fully-porous beads. Yang and Hu (1996) derived the theoretical expressions of elution and frontal linear chromatography for ion-exchange resins that were cored beads. Wang et al. (2007) studied the pressure-flow correlation with the ion-exchange resin of cored beads. They found that cored beads provided significantly enhanced rigidity and permeability compared to fully-porous homogeneous agarose beads (Luo et al., 2013). Gu et al. (2011) used the general rate model to study the optimization of the core radius fraction for multi-component isocratic elution with cored beads.

Analytical solutions and temporal moments of the 1D-models have been derived for linear isotherms using the Laplace transformation (Javeed et al., 2013; Qamar et al., 2013, 2015, 2014b; Leweke and von Lieres, 2016; Bibi et al., 2015). 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 times, band broadenings, and front asymmetries. Several authors have derived moments for various boundary conditions (BCs) (Javeed et al., 2013; Qamar et al., 2013, 2015, 2014b; Leweke and von Lieres, 2016; Bibi et al., 2015; Guiochon et al., 2006; Kubin, 1965a, 1965b; Kucera, 1965; Miyabe and Guiochon, 2000, 2003; Miyabe, 2007, 2009; Ruthven, 1984; Schneider and Smith, 1968; Suzuki and Smith, 1971; Suzuki, 1973; Wolff et al., 1980a,b).

Recently, we have also derived analytical solutions and temporal moments of linear 2D-models for cylindrical columns packed with fully-porous particles (Qamar et al., 2014a, 2017; Parveen et al., 2015, 2016). Very recently, Qamar et al. (2015, 2016) have investigated linear and nonlinear 1D-models for core–shell particles. However, 2D-models have never been analyzed before for cylindrical columns packed with core–shell particles. This article extends the works carried out in Qamar et al. (2015, 2016) for 1D-models to linear and nonlinear 2D-GRMs considering core–shell particles.

For nonlinear adsorption equilibria the column model equations need to be solved numerically. The finite volume schemes have been widely applied to numerically approximate different chromatographic models and have been found suitable for simulating such nonlinear convection dominated problems (Lieres and Andersson, 2010; Webley and He, 2000; Javeed et al., 2011; Qamar et al., 2016). These schemes were initially introduced for nonlinear hyperbolic equations. The slopes or flux limiters of these numerical schemes avoid numerical oscillations and over-predictions in the solutions and, thus, have capability to produce stable and accurate results (LeVeque, 1992).

In this article, analytical solutions and moments are derived for a linear single-solute 2D-GRM to study the effects of different kinetic parameters, especially the effects of radial dispersion on the elution profiles. Furthermore, the nonlinear multi-component 2D-GRM for core–shell particles is numerically approximated. A high resolution finite volume scheme, presented in Javeed et al. (2011), Qamar et al. (2016) for the 1D-models, is extended to solve the current 2D model equations.

2D models can be valuable in various situations, e.g. (a) the injection at the column inlet is not perfect (i.e. a radial profile is introduced at the column inlet), (b) the column is not homogeneously packed (which is more and more probable the larger the columns are), (c) there are radial temperature gradients, which are connected also with radial concentration gradients. All these issues occur in reality. Often they might be minor and even negligible, then justifying the 1D model. However, for evaluating the magnitude of the related effects 2D models are required. With already available isothermal models we could just study a special case for situation (a) by assuming injections in inner cylinders or outer annuli. Situations (b) and (c) are more complicated and require further model extensions (considering non-constant column porosities and an energy balance), which are currently under investigation. The already developed simplified 2D-models and numerical scheme are more general and flexible compared to the classical 1D-models and numerical schemes (Javeed et al., 2013, 2011; Qamar et al., 2013, 2015, 2014b; Leweke and von Lieres, 2016; Bibi et al., 2015).

The remaining parts of this article are organized as follows. In Section 2, the 2D-GRM model is introduced. In Section 3, the analytical solutions of a linear single-solute 2D-GRM are derived for the considered two sets of boundary conditions. In Section 4, the analytical temporal moments are derived. Section 5 explains the proposed finite volume scheme applied to solve the nonlinear 2D-GRM. In Section 6, several case studies are presented. Lastly, concluding remarks are given in Section 7.

2. The mathematical model of 2D-GRM

In liquid chromatography, the GRM considers several contributions of the mass transfer processes that lead to band broadening. Mass transfer between the stationary and mobile phases, axial dispersion, and intraparticle pore diffusion are incorporated in the mass balance equations.

Let t denotes the time coordinate, z represents the axial coordinate along the column length, and r is the radial coordinate along the 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 r-direction by radial dispersion. The following particular injection conditions are assumed to amplify the effects of mass transfer in the radial direction. A new parameter $\tilde{r}$ is introduced to split the inlet cross section of the column into an inner cylindrical core and an outer annular ring (see Fig. 1). Thus, sample can be injected to the column either through an inner, through an outer ring, or through the whole cross section. The latter case results if $\tilde{r}$ is set equal to the radius