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# Numerical simulation of nonlinear chromatography with core–shell particles applying the general rate model

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## HIGHLIGHTS

- Numerical solutions of nonlinear GRM for core–shell particles are presented.
- A semi-discrete high resolution finite volume scheme is applied.
- Potential of core–shell particles compared to fully porous particles is analyzed.
- Performance criteria are evaluated for finding optimum core radius fraction.
- Relevant results are obtained to understand and optimize the process.

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## ABSTRACT

Core–shell particles allow highly efficient and fast separation of complex samples. They provide advantages over fully porous particles, such as highly efficient separation with fast flow rate due to shorter diffusional path length in particle macropores. On the other hand, capacities are reduced due to the inert core. This work is focused on the numerical approximation of a nonlinear general rate model for fixed-beds packed with core–shell particles. The model equations consider axial dispersion, interfacial mass transfer, intraparticle diffusion, and multi-component Langmuir isotherm. A semi-discrete high resolution flux-limiting finite volume scheme is proposed to accurately and efficiently solve the model equations. The scheme is second order accurate in axial and radial coordinates. The resulting system of ordinary differential equations (ODEs) are solved by using a second-order TVD Runge–Kutta method. For illustration, a few selected scenarios of single solute and multi-component elution bands are generated to study theoretically the effects of the core radius fractions on the course of elution curves. Typically applied performance criteria are evaluated for identifying ranges of optimum values of the core radius fraction.

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## 1. Introduction

High performance liquid chromatography (HPLC) is considered to be an essential analysis tool for research, manufacturing, clinical tests, and diagnostics. The current trends in HPLC are towards achievement of higher kinetic efficiency, shorter analysis time and low back pressure for various types of samples. In efforts to increase the power of HPLC, the particles packed into the columns have been progressively improved and downsized. The

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development of ultra-high-performance liquid chromatography (UHPLC) using such smaller particles has made possible to enhance the good analytical features of HPLC and to improve the column performance. However, despite the fact that UHPLC allows efficient and fast separations and utilizes smaller amounts of solvents, the small sized particles put an extra burden on HPLC instrumentation, see [Salisbury \(2008\)](#). The invention of core beads (also known as pellicular, superficially porous, and fused-cored beads or particles) has introduced an alternative technology which avoids the use of special equipments. Their efficiency is comparable to UHPLC and have low back pressures, see [Kirkland et al. \(2000\)](#), [Fanigliulo et al. \(2010\)](#), and [Pietrogrande et al. \(2010\)](#). They also provide the possibility of using already existing conventional

HPLC systems in the laboratories, see Ali et al. (2012).

Cored beads are made of a solid core surrounded by a porous layer having essentially the properties of porous particles used in conventional HPLC columns, see Horvath et al. (1967), Pesek and Frost (1973), Ning et al. (1998), Coutinho et al. (2001), Greibrokk (2004), Kirkland et al. (2000, 2007), Zhou et al. (2007), Kiss et al. (2010), Manchon et al. (2010), Gritti et al. (2010), Gritti and Guiochon (2010), Guiochon and Gritti (2011), Spudeit et al. (2014), Hayesa et al. (2014), Lambert et al. (2014), González-Ruiz et al. (2015), and Horváth and Felinger (2015). They were introduced to build highly efficient HPLC columns for separating the constituents of high molecular weight compounds of biological origin, see e.g. Horvath et al. (1967). They offer advantages over fully porous beads, such as highly efficient separation with fast flow rate due to shorter diffusional path length in particle macropores. For compounds having high internal mass-transfer resistance, the gain in efficiency compensates the reduction in sample capacity due to the lower volume of porous adsorbent, see Kaczmarski and Guiochon (2007). On the other hand, the gain decreases with decreasing mass-transfer resistance, for instance with decreasing molecular weight of the compound.

In HPLC, the use of cored beads is a compromise between fully porous beads and non-porous beads, see Wang et al. (2006). Non-porous beads eliminate intraparticle diffusion and generate sharp elution peaks of the shortest retention times, see Lee (1997), Rissler (2000), Xiang et al. (2003), Fekete et al. (2010), and Gu et al. (2011). However, they are unable to provide sufficient retention time range in HPLC due to their limited binding capacities, see e.g. Kirkland et al. (2000) and Miyabe (2008). In contrast, fully porous beads offer the largest retention time differences, but suffering from excessive band broadening. Fanigliulo et al. (2010) and Cabooter et al. (2010) performed experiments to compare and analyze several commercially available fully porous and cored beads.

Mathematical modeling of the dynamic chromatographic process is an important ingredient of the chromatography theory. It offers a technique for predicting the dynamic behaviors of the solute in the columns without extensive experiments. Because of different levels of complexity, several models have been established and applied in the literature, see Ruthven (1984), Carta (1988), Guiochon (2002), and Guiochon and Lin (2003). Among them, the General Rate model (GRM) is the most complicated and complete. It includes most of the factors which influence mass transfer process in the column, such as the axial dispersion, external mass transfer resistance, pore diffusion, surface diffusion and adsorption/desorption kinetic procedure. Thus, GRM possesses the potential to include more kinetic resistances, which makes it more realistic. For certain limits of transport parameters it converges into the LKM, see Guiochon et al. (2006). Zhou et al. (2007) used a general rate model for cored beads to obtain intraparticle diffusion coefficients. Kaczmarski and Guiochon (2007) considered thin-shelled coated beads using a lumped particle model. They assumed that the concentration profile inside the thin shell could be expressed by a single averaged concentration value. For comparison with fully porous beads, they used the general rate model for fully porous beads. Li et al. (2010) performed optimization of core size for linear chromatography by minimizing height equivalent theoretical plate (HETP) number. Gu et al. (2011) have presented a nonlinear general rate model for cored beads and its numerical solution strategy. The model was used to optimize the core radius fraction for a preparative ternary elution system as an example case. Luo et al. (2013) have simulated cored beads for size-exclusion chromatography using the general rate model (GRM). Li et al. (2003a) have used GRM and Langmuir isotherm to analyze adsorption/desorption kinetics of protein on the binding ligand of inert core adsorbent. Moreover, Li et al. (2003b, 2004)

have derived analytical solution of the linear GRM to predict breakthrough curves for the inert core adsorbent. Core-shell particles find one real application at industrial scale on expanded bed adsorption for protein capture. The use of similar model and application has been discussed by Li et al. (2005, 2006).

This paper is concerned with the numerical approximation of a nonlinear GRM for core-shell particles. It is an extension of our recent work on the analysis of linear GRM for core-shell particles, see Qamar et al. (2015). For nonlinear adsorption isotherms, analytical solutions of the model equations are not possible. For that reason, numerical simulations are required to accurately predict the dynamic behavior of chromatographic columns. Steep concentration fronts may occur because of the convection dominated partial differential equations (PDEs) of the chromatographic models. Thus, efficient and accurate numerical method is required to study dynamics in chromatographic columns packed with core-shell particles. The model considers multi-component mixture, axial dispersion, interfacial mass transfer, intraparticle diffusion, and nonlinear adsorption. A high resolution flux-limiting finite volume scheme is suggested to solve the model equations. The accuracy and efficiency of this scheme for equilibrium dispersive model was recently tested by Javeed et al. (2011). In that article, it was found that the proposed scheme is simple, accurate, and easy to implement as compared to other high resolution finite volume and finite element methods applied to the same model equations. Different case studies of the one-, two-, and three-component mixtures are considered. With these case studies it is intended to analyze the effects of core radius fraction, axial dispersion, film mass transfer resistance and intraparticle diffusion resistance, on the elution curves. Assessment criteria are introduced to understand the process and to optimize the core size for achieving maximum productivity. A comparison of linear and nonlinear cases is presented to reveal the effects of nonlinearity. The tools developed and the simulation results generated should be helpful to synthesize tailor-made particles.

This article is arranged as follows. In Section 2, the nonlinear general rate model using cored beads is briefly introduced. In Section 3, the proposed accurate and efficient numerical scheme is derived and criteria to evaluate the performance of preparative chromatography are introduced. In Section 4, several case studies are carried out which are helpful in rationally designing thicknesses of shell layers for preparative applications. Finally, conclusions are drawn in Section 5.

## 2. Mathematical model for core beads

An isothermal adsorption column packed with inert core particles is considered as shown in Fig. 1. At time zero, a step change in the concentration of an adsorbate is introduced in a flowing stream. The adsorption column is subjected to axial dispersion, film mass transfer resistance and intraparticle diffusion resistance. It is assumed that cored beads have uniform particle size  $R_p$  and core size  $R_{core}$ . The inner core cannot be penetrated and there is only diffusion (no convection) in the porous shell. The column is considered to be isothermal.

Under these assumptions, the mass balance equations for a multi-component mixture of  $N_c$  components percolating through a column filled with spherical core beads of radius  $R_p$  are given as (c.f. Guiochon, 2002; Guiochon et al., 2006)

$$\frac{\partial C_{b,i}}{\partial t} + u \frac{\partial C_{b,i}}{\partial z} = D_{b,i} \frac{\partial^2 C_{b,i}}{\partial z^2} - \frac{3}{R_p} F_b k_{ext} (C_{b,i} - C_{p,i}|_{r=R_p}),$$

$$i = 1, 2, \dots, N_c. \quad (1)$$

In the above equation,  $C_{b,i}$  and  $C_{p,i}$  are the concentrations of  $i$ th

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