Computational investigation of longitudinal diffusion, eddy dispersion, and trans-particle mass transfer in bulk, random packings of core–shell particles with varied shell thickness and shell diffusion coefficient[☆]

Anton Daneyko[a], Dzmitry Hlushkou[a], Vasili Baranau[a], Siarhei Khirevich[a], Andreas Seidel-Morgenstern[b], Ulrich Tallarek[a,*]

[a] Department of Chemistry, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, 35032 Marburg, Germany
[b] Max-Planck-Institut für Dynamik komplexer technischer Systeme, Sandtorstrasse 1, 39106 Magdeburg, Germany

ABSTRACT

In recent years, chromatographic columns packed with core–shell particles have been widely used for efficient and fast separations at comparatively low operating pressure. However, the influence of the porous shell properties on the mass transfer kinetics in core–shell packings is still not fully understood. We report on results obtained with a modeling approach to simulate three-dimensional advective–diffusive transport in bulk random packings of monosized core–shell particles, covering a range of reduced mobile phase flow velocities from 0.5 up to 1000. The impact of the effective diffusivity of analyte molecules in the porous shell and the shell thickness on the resulting plate height was investigated. An extension of Giddings' theory of coupled eddy dispersion to account for retention of analyte molecules due to stagnant regions in porous shells with zero mobile phase flow velocity is presented. The plate height equation involving a modified eddy dispersion term excellently describes simulated data obtained for particle-packings with varied shell thickness and shell diffusion coefficient. It is confirmed that the model of trans-particle mass transfer resistance of core–shell particles by Kaczmarski and Guiochon [42] is applicable up to a constant factor. We analyze individual contributions to the plate height from different mass transfer mechanisms in dependence of the shell parameters. The simulations demonstrate that a reduction of plate height in packings of core–shell relative to fully porous particles arises mainly due to reduced trans-particle mass transfer resistance and transchannel eddy dispersion.

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1. Introduction

Core–shell particles have recently been intensively studied and employed for highly efficient, fast separations [1–16]. They consist of a nonporous fused-silica core surrounded by a porous layer having essentially the properties of fully porous particles. The performance of columns packed with sub-3 μm core–shell particles challenges that of columns packed with sub-2 μm fully porous particles, with the advantages of operating at back-pressures close to 3 μm-particle packings and smaller efficiency losses due to thermal effects at high flow rates [2,17–19]. The efficiency of a column

with a given length and bed characteristic scale is inversely proportional to its height equivalent to a theoretical plate (HETP), which is mainly a function of the linear velocity of the mobile phase during an isocratic run. Nearly 60 years ago, van Deemter et al. [20] have formulated an empirical equation describing the essence of band broadening in chromatographic columns. These authors simplified the solution of the kinetic model developed earlier by Lapidus and Amundson [21] by assuming a Dirac pulse shape of the injection pulse. They established that the broadening of an analyte band during its migration along the column and the HETP are controlled by three independent factors: (i) longitudinal diffusion of analyte molecules along the concentration gradient in the eluent, (ii) eddy dispersion due to sample transport and exchange between the anastomosed flow paths in a packed bed, and (iii) mass transfer resistance due to finite rates for the transfer of analyte molecules between bulk eluent and stationary phase. These contributions to

the HETP are referred to in chromatography as, respectively, the B, A, and C terms (or coefficients) of the van Deemter equation

$$H = \frac{B}{u_{av}} + A + Cu_{av}, \tag{1}$$

where H is the plate height and u_{av} the average mobile phase velocity. The three contributions to the HETP account for all the band broadening due to mass transfer processes encountered in any type of chromatographic column. For instance, the B term is related to an apparent, complex diffusion coefficient accounting for the sample diffusivity in the interparticle bulk eluent and in the pore network of the stationary phase. The A term includes contributions due to flow velocity biases taking place over different characteristic lengths in the column, which can be divided into transchannel (associated with the dimension of the interparticle channels between neighboring particles), short-range interchannel (associated with the scale of a few particle diameters), long-range interchannel (associated with the distances between local defects in a packing), and transcolumn effects (associated with heterogeneities at the scale of the column dimension) [22]. The flow velocity biases behind the two latter contributions (long-range interchannel, transcolumn) occur only in macroscopically inhomogeneous packed beds. The C term accounts for all mechanisms resulting in a finite response time that analyte molecules need for transfer between solid and bulk liquid phase. As a consequence, the coefficients in Eq. (1) are semi-empirical and cannot be related directly to a physical description of the individual mass transfer mechanisms. A comprehensive approach to the efficiency of chromatographic beds therefore must distinguish between the individual contributions to band broadening arising from different mass transfer mechanisms and physiochemical phenomena. Then, the general HETP equation can be written as [23]

$$H = H_{long} + H_{eddy} + H_{film} + H_{stat} + H_{ads} + H_{fe}, \tag{2}$$

where the subscripts "long", "eddy", "film", "stat", "ads", and "fe" denote the contribution of longitudinal diffusion, eddy dispersion, external film mass transfer resistance, mass transfer resistance across the stationary phase including pore and surface diffusion, the rate of adsorption–desorption at the surface of an adsorbent, and the friction–expansion of the mobile phase, respectively.

Using peak parking experiments with a diffusion model based on the effective medium theory, Gritti and Guiochon [24] analyzed individual contributions to band broadening in columns packed with Halo and Kinetex core–shell particles. They demonstrated that the high efficiencies for core–shell particles in resolving low molecular weight compounds result from a combination of a smaller longitudinal diffusion term (B term in Eq. (1) and H_{long} term in Eq. (2)) and significantly reduced eddy dispersion (A term in Eq. (1) and H_{eddy} term in Eq. (2)) compared to those in columns packed with conventional fully porous particles [4,24]. Later, numerical simulations of hydrodynamic dispersion in bulk random packings of polydisperse particles [25] and the morphological analysis of physically reconstructed packed beds [26] revealed that the smaller eddy dispersion contribution to band broadening in columns packed with core–shell particles should be attributed to a higher transcolumn homogeneity rather than an improved bed morphology on smaller length scales. The origin for the decrease of B and H_{long} terms can be explained by a reduction of the total packed-bed volume accessible for diffusion due to the presence of the particles' solid cores. However, a rigorous theoretical analysis of the interrelation between physico-chemical properties of the porous shells, analyte molecules, and column efficiency is still an unresolved problem.

The theoretical determination of the terms in the HETP equations is generally a big problem as it requires resolvable and accurate mathematical models for all mass transfer phenomena occurring in chromatographic columns. The greatest challenge results from the random and heterogeneous nature of the packed particulate beds. In this regard, computer simulations provide the exceptional possibility to evaluate the mass transfer characteristics in packed beds and analyze systematically the dependence of separation efficiency on individual parameters of the chromatographic system.

In this contribution, we present the results of a numerical investigation of advective–diffusive mass transfer in bulk random packings of spherical core–shell particles. We analyze the impact of the effective diffusivity of analyte molecules in the porous shell as well as the shell thickness on the plate height. For this purpose, we computer-generated random packings of monosized particles. Then, we computed the three-dimensional flow velocity field in the interparticle void space using the lattice-Boltzmann method (LBM). Finally, the transport of point-like tracers in the interparticle void space and porous shells of the packing particles was modeled by a random-walk particle-tracking (RWPT) technique. A similar simulation approach was previously applied to study the effect of packing porosity, morphology, and particle size distribution on effective diffusivity and eddy dispersion in packed beds [25,27–31]; to analyze the impact of the packing confinement on eddy dispersion [32,33]; to study hydrodynamic dispersion in silica and polymeric chromatographic monoliths [34–38]; and to investigate the influence of analyte retention and adsorption kinetics on mass transport in open channels and packed beds [39–41]. In this study, we mainly focus on the analysis of the influence of two core–shell particle characteristics – the shell thickness and the value of the effective diffusion coefficient in the shell – on the plate height. The plate height equation for the system we investigate consists of three terms

$$H = H_{long} + H_{eddy} + H_{stat}, \tag{3}$$

where the H_{eddy} term is associated with the flow velocity biases on only the transchannel and short-range interchannel characteristic lengths, because the packings are bulk packings, i.e., unconfined (no wall effects) and macroscopically homogeneous. The H_{long} term associated with the apparent diffusivity of tracers in the entire packing (including the interparticle void space and pore network in the particles' porous shells) is obtained by the RWPT simulation in the absence of flow. Then, we determine the plate height at different mobile phase flow velocities (with reduced velocities between 0.5 and 1000), while keeping the same structure of the packing, and vary the following two parameters: the diameter of the particles' solid core from zero (fully porous particles) to the particle diameter (nonporous particles) and the value of the effective diffusion coefficient in the porous shells. We analyze individual contributions to the plate height arising from different mass transfer mechanisms, using a proposed extension of the Giddings coupled eddy dispersion model to packings of core–shell particles and the model of Kaczmarski and Guiochon [42] originally developed for mass transfer in a single core–shell particle.

2. Numerical methods

2.1. Overview of the employed simulation methods

The numerical simulations of mass transport in packings of core–shell particles as performed in this work involve three distinct methods: (i) simulation of the bed structure, (ii) simulation of fluid flow in the interparticle void space, (iii) simulation of advective–diffusive transport of inert (non-reactive) point-like tracers. Firstly, a collective-rearrangement algorithm based on the Jodrey–Tory method was employed to generate random packings of spheres (Section 2.2). The method reproduces the morphological