Journal of Chromatography A, 1407 (2015) 69–75

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Predictive model of solute transport with reversible adsorption in spatially periodic hierarchical porous media

Xiaohong Yan[a,*], Qiuwang Wang[b], Nan Li[c]

[a] *Department of Chemical Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, China*
[b] *Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, China*
[c] *Xi'an Haitang Vocational College, Xi'an, Shaanxi, 710049, China*

ARTICLE INFO

Article history:
Received 15 April 2015
Received in revised form 8 June 2015
Accepted 9 June 2015
Available online 17 June 2015

Keywords:
Transport
Hierarchical porous
Adsorption
Volume average
Multiscale

ABSTRACT

Solute transport in hierarchical porous media with reversible adsorption is predicted by the volume averaging method. A transient macroscopic advection-diffusion equation is derived to describe the multiscale solute transport problem. The theoretical expression of the dispersion tensor is obtained which is the function of pore-scale velocity profile. Steady closure equations are derived to calculate the dispersion tensor. With the aid of pore-scale simulation in unit cells of the hierarchical porous media, the dispersion tensor can be calculated. The model is verified by comparing its predictions and obtaining favorable agreement with results of direct numerical simulations and with experimental data for columns comprised of ordered, porous pillars. It is straightforward to use the model to predict the solute transport behavior in fixed beds packed with particles.

1. Introduction

Columns packed with porous particles are widely used in industrial devices, such as the chromatography columns [1], fixed bed adsorption devices [2], packed bed reactors [3]. These columns can be considered as porous media with hierarchical pore structure (inter-particle macropores and intra-particle micropores). Hierarchical porous media provide large surface areas for reaction or adsorption. When these devices are applied for solute separation or reaction, the solvent is present in both the macropores and micropores. Driven by pressure, the solvent in the macropores is free to move. Mass transfer in the macropores takes place by both advection and diffusion. The micropores are sufficiently small to suppress any appreciable fluid motion. Hence, mass transfer in the micropores occurs by diffusion. The surface of the micropores is coated with a thin stationary phase. Adsorption and desorption occur at the stationary phase. The solute transport behavior has profound effects on the process performance. For example, in chromatographic separation, smaller solute transport resistance results in better separation resolution [4,5].

The solute transport process depends on the hierarchical pore geometry of the hierarchical porous media. Hence, various methods have been developed to prepare hierarchical porous media with tunable pore geometry and pore size, such as core-shell particle packs [6,7], array of pillars with porous shell [8], metal-organic frameworks with tunable macropore size [9], nanopillar array [10,11], porous graphitic carbon [12].

The ability to theoretically predict the multiscale solute transport process would be helpful not only to obtain a deeper understanding of related process performance, but also to promote the design of novel separation columns or reactor with desired properties. This is particularly important in view of recent advances in microfabrication technologies which facilitate the fabrication of porous media comprising of ordered pillar arrays [8,10], three dimensional ordered hierarchical porous materials [9]. Since available techniques provide the designer with the flexibility of forming multiscale pore geometry of various shapes and patterns, one has the opportunity to optimize chromatography column and reactor design and significantly improve the process performance.

Most theoretical and experimental works addressing solute transport in porous media have focused on porous media comprising impermeable particles, pillars or monoliths [4,13–20]. Perhaps due to their complex pore geometry, experimental and theoretical predictions of solute transport in hierarchical porous media are few. Transient and asymptotic dispersion behaviors in columns packed with porous particles (or double porosity porous media) were studied experimentally and models were used to understand these behaviors [21–26]. Magnico et al. [21] reported that the axial dispersivity (axial dispersion coefficient/average velocity) for double porosity porous media increases faster with velocity

---

[*] Corresponding author. Fax: +86 29 82663502.
E-mail address: xhyan11@mail.xjtu.edu.cn (X. Yan).

http://dx.doi.org/10.1016/j.chroma.2015.06.019
0021-9673/

than for single porosity porous media. They also revealed that non-Gaussian dispersion behavior can be observed when the transit time inside individual grains becomes of the order of the mean transit time across the whole sample. Papathanasiou and Bijeljic [22] experimentally and Bijeljic et al. [23] theoretically analyzed tracer tailing in breakthrough curves in columns packed with solid and porous beads based on experimental measurements and the Continuous Time Random Walk (CTRW) method. They demonstrated that breakthrough curves for a column containing solid glass beads exhibit non-Fickian transport. They also revealed that the presence of porous beads introduces a second spatial/time scale and the extent of tailing is much stronger, which can be quantified by a two-scale CTRW model. Drazer et al. [24] reported a method based on radioactive dispersion experiment and the Coats-Smith model to determine characteristic exchange time between the internal and external pores, mean tracer velocity, mobile fluid fraction and longitudinal dispersion coefficient for tracer dispersion in double porosity activated carbon packings. Tallarek et al. [25] investigated the mass transfer in chromatographic columns packed with spherical-shaped, porous particles by the pulsed field gradient nuclear magnetic resonance technique. They revealed the existence of external stagnant fluid where all the interparticle fluid-side resistance to diffusion is localized. They demonstrated that the actual correlation (or randomness) of interconnection between intraparticle pores of different size has a profound effect on the observed tortuosity factors and the diffusion-limited stagnant mobile phase mass transfer kinetics. Kandhai et al. [26] used pulsed field gradient nuclear magnetic resonance (PFG-NMR) and lattice-Boltzmann (LB) algorithm investigated the solute dispersion in a column packed with porous particles. Results demonstrated that intraparticle liquid holdup in macroscopically homogeneous porous media clearly dominates over contributions caused by the intrinsic flow field heterogeneity and boundary-layer mass transfer in a random packing of porous spheres with column-to-particle diameter ratio above 100. Computational software and hardware advances make it possible to do pore-scale simulation in hierarchical porous media. Some researchers have resorted to direct pore-scale numerical simulations [27–30]. Simulation results significantly improve our understanding of the solute transport in both macropores and micropores. Unfortunately, the influence of micropore geometry on the macroscopic transport behavior is still difficult to be investigated by the direct pore-scale simulation.

A useful alternative consists of models that allow one to determine effective solute transport properties with various homogenization techniques [31–36]. Such models may still require numerical computations, but these computations are restricted to representative element volume and are manageable with modest computational resources. Quintard and Whitaker [34] established a model to describe the transport of an adsorbing solute in a two-region model of heterogeneous porous media. Three geometric scales exist in the heterogeneous porous media. The small scale and Darcy scale correspond to the micropore scale and macropore scale of current hierarchical porous media, respectively. The large scale corresponds to the scale of the heterogeneous region. The model for the small scale and Darcy-scale describes the similar physical problem as we considered here. A macroscopic equation and related closure equations were derived based on the assumption of the local mass equilibrium. Perhaps due to the complex closure equations (integro-differential equations) and the lack of detailed model validation, the model has not been used to predict the solute transport in chromatography applications.

Recently, Yan et al. [16] used the volume averaging method to derive an expression for the plate height in pillar arrays consisting of solid (impermeable) pillars with wall retention. Their theoretical predictions provided an excellent agreement with available experimental data and with results of direct numerical simulations. In this paper, we expand the earlier work of Yan et al. [16] to derive a theoretical model for solute transport in hierarchical porous media without local mass equilibrium assumption and derive simpler closure equations than Quintard and Whitaker [34] and compare the model's prediction results with available numerical and experimental results for chromatography applications.

The paper is organized as follows. Section 2 introduces the theoretical model. Section 3 verifies the model by comparing its predictions with results of direct numerical simulations and with available experimental data. Section 4 concludes.

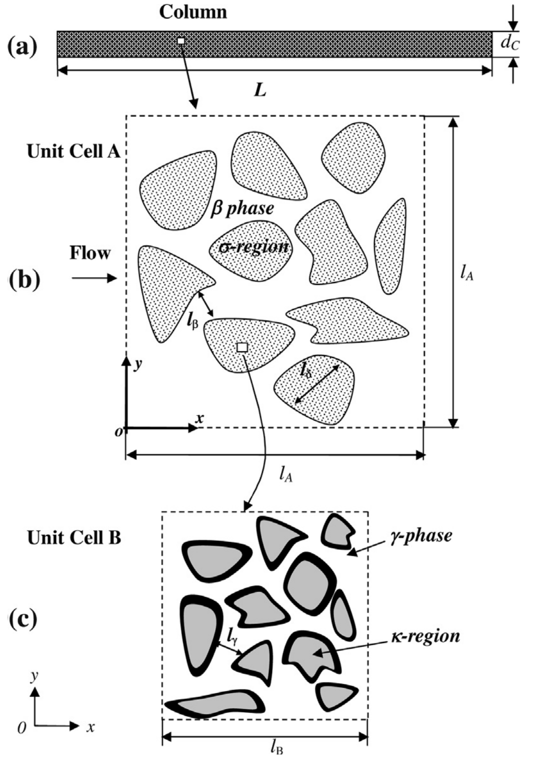

Fig. 1. (a) The column with a representative unit cell A. (b) Enlarged view of unit cell A and depiction of unit cell B. (c) Enlarge view of unit cell B. The x-coordinate is aligned with the column's axis. The z-coordinate points out of the page.

2. Theoretical model

Consider a column of length L and effective diameter d_C (Fig. 1a). The column is filled with hierarchical porous media (Fig. 1). The solvent is present in both the macropores (β-phase) and micropores (γ-phase). The solvent in macropores is free to move. Mass transfer in the β-phase takes place by both advection and diffusion (Fig. 1b). We consider the situation that micropores are sufficiently small to suppress any appreciable fluid motion. Mass transfer in the γ-phase occurs by diffusion alone. The surface of the pores is coated with a *thin* stationary phase (Fig. 1c). The solute can migrate back and forth between the stationary phase and the γ-phase. The adsorption and desorption can be described by a linear adsorption isotherm. The geometric scales are shown in Fig. 1. $L \gg l_A \gg l_\beta$, $l_\beta \approx l_\sigma$, and $l_B \gg l_\gamma$.

We consider pressure-driven flow of incompressible solvent laden with solutes. The solutes are dilute, do not affect the solvent's properties, and do not interact. Consequently, we treat each solute as if it exists all by itself. The fluid motion is described by the Navier-Stokes equation. The solvent obeys nonslip boundary conditions at all solid boundaries.