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Comparative analysis of chromatography dynamic models in predicting the plate height contributed by interphase mass transfer

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HIGHLIGHTS

- The accuracy of a specific general rate model applied in three cases is discussed.
- Retention factor dependence of plate height reported previously can be improved.
- The general rate model is accurate for flow with uniform velocity profile.
- The accuracy of the general rate model depends on the retention factor and velocity.
- Volume averaging model is more accurate than a general rate model for some cases.

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ABSTRACT

The accuracy of the general rate model and the volume averaging model was checked by comparing their predicted plate height contribution from the external (film) mass transfer with that predicted by the direct numerical simulation. Plug flow through open column, pressure driven flow through columns packed with pillar array, ordered spherical particles were considered as special cases. Results show that the general rate model is accurate for plug flow through open columns but inaccurate for pressure driven flow cases. The volume averaging model is accurate for both the plug flow and pressure driven flow cases. A retention factor dependence of the plate height being different from that derived from the general rate model was proposed to accommodate general flow conditions.

1. Introduction

With the development of microfabrication technology, columns with extremely high performance have been fabricated, such as the column packed with microscale ordered pillars (De Malsche et al., 2012) and the column packed with nanoscale ordered particles (Wei et al., 2012). The design and optimization of such high performance chromatography columns call for accurate interpretation of the band broadening process.

The general rate model and several simplified models are widely used to describe the mass transfer process in packed columns (Chan et al., 2008; Feist et al., 2009; Gritti and Guiochon, 2006, 2011; Gu et al., 2011; Kiss et al., 2010; Liu et al., 2010; Nagrath et al., 2004, 2011). The complex transport phenomenon in packed columns is described by several one dimensional equations in the model. Using the method of moments, researchers derived the plate height expression based on the general rate model (Gritti and Guiochon, 2006). The plate height expression describes separate contributions of the longitudinal dispersion, the external (film) mass transfer and the intraparticle diffusion to the band broadening process, which provides more detailed information than other plate height expressions involving many empirical constants (Giddings, 1965; Knox, 1999; Van Deemter et al., 1956).

Several works related to the general rate model have been reported recently. Von Lieres and Andersson (2010)developed a new solver to improve the accuracy and reduce the computational time of the simulation. Gritti and Guiochon (2010) discussed the methods on the determination of parameters involved in the model. Several researchers checked the accuracy of the external (film) mass transfer coefficient correlation in liquid chromatography (Deridder and Desmet, 2012; Miyabe et al., 2008, 2010a, 2010b). The group of Guiochon carried out a series of research (Miyabe et al., 2008, 2010a, 2010b) to check the validity of external (film) mass transfer coefficient correlations reported in literature. The external (film) mass transfer

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coefficient was measured in HPLC systems for columns packed with nonporous spherical particles (Miyabe et al., 2008), fully porous spherical particles (Miyabe et al., 2010a) and a monolithic column (Miyabe et al., 2010b). The Reynolds number was smaller than 0.05 and the Schmidt number was varied from 1800 to 2700. They concluded that conventional literature correlations (Kataoka et al., 1972; Pfeffer, 1964; Wilson and Geankopolis, 1966) provided a correct estimation of the external (film) mass transfer coefficient in HPLC systems. Deridder and Desmet (2012) simulated the mobile zone mass transfer in a variety of ordered structures and calculated the external (film) mass transfer coefficient. The numerical results suggested that the external (film) mass transfer coefficient for several columns could not be correctly predicted by those widely used correlations (Kataoka et al., 1972; Pfeffer, 1964; Wilson and Geankopolis, 1966). New correlations were proposed. Note that the general rate model is not a single model, several researchers developed many different versions of general rate models (Berninger et al., 1991; Ma et al., 1996; Nagrath et al., 2004, 2011).

Despite the progress on the general rate model, the fundamental research on the general rate model is rare. Desmet and Broeckhoven (2008) discussed available expressions of plate height caused by the external (film) mass transfer and intraparticle diffusion. Their study revealed that there was a uniform velocity profile assumption underlying the general rate model. This assumption is in contradiction of the practical situation of packed columns, but the general rate model is widely used to predict the elution process and the plate height of packed columns.

We established one model based on the volume averaging method to account for the effects of the axial dispersion and the external (film) mass transfer on the band broadening (Yan et al., 2010). The model is only applicable for columns packed with nonporous particles or pillars, but the model has some advantages over the general rate model. The parameters in the equation of the general rate model, such as the longitudinal dispersion coefficient and the external (film) mass transfer coefficient, can not be determined by the model itself, while all parameters in the equation of the volume averaging method model can be solved by the closure equations in the model. The effect of the column geometry on the band broadening can not be accounted for by the general rate model itself but can be accounted for by the volume averaging method model. The model was consistent with available results of open columns and was validated for columns packed with ordered pillars.

Despite the wide application of the general rate model, the effect of the underlying uniform velocity profile assumption remains unchecked. Although the volume averaging model is derived without the uniform velocity profile assumption, the accuracy of the model for predicting the plate height in particle packed columns is unknown and thus the application of this model is rare. The objective of this study is to theoretically check the accuracy of the general rate model and the volume averaging model for predicting the plate height of open columns and columns packed with ordered pillars or particles.

2. Methods

In order to achieve the objective, we employed the plate height calculated by the direct numerical simulation to act as the “numerical experimental result” and which was compared with that calculated by the general rate model and the volume averaging model. The model predicting the same result as the “numerical experimental result” is the accurate model.

2.1. The physical problem and considered geometries

For typical chromatographic columns, the column length is long enough to achieve the asymptotic values of the dispersion coefficient and the plate height, thus we focus on the asymptotic value of the plate height. We considered a special type of columns: there is a thin stationary phase coated on the surface of the open column or the surface of nonporous pillars or particles of the packed columns and the adsorption rate is fast enough (Suzuki, 1990).

Only the open column and the column packed with nonporous ordered pillars or particles were considered for the following reasons: (1) the currently available volume averaging model is applicable for such columns; (2) detailed expressions of the external (film) mass transfer coefficient for such columns are available; (3) the stationary phase is a thin layer at the surface of open columns or pillars or particles, and thus the mass transfer inside the stationary phase is negligible and the concentration inside is unifrom if the stationary phase is thin enough, so the direct numerical simulation is possible; (4) to achieve the objective of this study, the main focus is the effect of the velocity profile in the mobile phase, and the usage of such columns has no influence on the final objective.

The band broadening in such columns is caused by two types of factors: (1) the longitudinal dispersion, which includes effects of the longitudinal diffusion and the nonuniform velocity profile (in some literatures, it is called eddy dispersion or eddy diffusion), and (2) the external (film) mass transfer or interfacial mass transfer between the mobile phase and the stationary phase. Because both the longitudinal dispersion coefficient and the external (film) mass transfer coefficient can not be predicted by the general rate model, the main contribution of the general rate model to the plate height expression is the explicit retention factor dependence of the plate height contribution from the external (film) mass transfer. Therefore, we compared the plate height component that contributed from the external (film) mass transfer to check the accuracy of the general rate model and the volume averaging model.

The circular open column (column I), columns filled with pillar array (column II), spherical particles in the face-centered cubic arrangement (column III) were considered. Part of the internal geometry of column II and column III is shown in Fig. 1a, which is also the computational domain of the direct numerical simulation. Unit cells of column II and column III are shown in Fig. 1b, which is the computational domain of the volume averaging model. The molecular diffusion coefficient is 1×10^{-9} m^2/s. The diameter of the open column, pillars and particles is 5 μm, and the porosities of the two columns packed with pillars and particles are 0.4 and 0.38, respectively. In the direct numerical simulation, two values of the retention factor, 1 and 10, were considered. The dimensionless interstitial velocity is controlled from 1 to 50. The numerical simulation is done by the COMSOL Multiphysics software.

2.2. The general rate model and the physical meaning of the external (film) mass transfer

The governing equation of solutes in the mobile phase is

$$\frac{\partial C}{\partial t}+u_{\mathrm{i}}\frac{\partial C}{\partial x}=D_{\mathrm{L}}\frac{\partial^2 C}{\partial x^2}-\frac{1-\varepsilon}{\varepsilon}k_{\mathrm{ext}}\frac{A_{\mathrm{p}}}{V_{\mathrm{p}}}\left(C-\frac{C_{\mathrm{s}}}{K}\right) \tag{1}$$

note that the concentration in the equation should be considered as the average concentration of the unit cell of the column. The unit cell is one slice of the column. The effect of the velocity distribution and local concentration distribution is taken into account by two velocity-dependent parameters, the longitudinal dispersion coefficient and the external (film) mass transfer coefficient.

Considering the mass transfer in the unit cell, we know that the flux caused by the external (film) mass transfer equals the integrated diffusive flux through the mobile phase-stationary