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On the optimisation of the bed porosity and the particle shape of ordered chromatographic separation media

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Abstract

We report on a theoretical study wherein we considered a large number of ordered two-dimensional porous pillar arrays with different pillar shapes and widely varying external porosity and calculated the flow resistance and the band broadening (under retentive conditions) over the complete range of practical velocities using a commercial computational fluid dynamics software package. It is found that the performance of the small porosity systems is very sensitive to the exact pillar shape, whereas this difference gradually disappears with increasing porosity. The obtained separation impedances are very small in comparison to packed bed and monolithic columns and decrease with increasing porosity. If accounting for the current micromachining limitations, a proper selection of the exact shape and porosity even becomes more critical, and different design rules are obtained depending on whether porous or non-porous pillars are considered.

Keywords: Band broadening; Etched columns; Computational fluid dynamics

1. Introduction

The packed bed of spheres, with its fixed particle shape and fixed external bed porosity (around $\varepsilon = 0.4$), has for many decades been the undisputed chromatographic column format. Since the introduction of radically new column manufacturing concepts, cf. the various sol–gel techniques used for the preparation of monolithic packing structures [1–5] and the micromaching techniques Regniers' group [6–8] used to produce their collocated monolithic support structures (COMOSS) column, the bed porosity and the particle shape have become important new design parameters. With appropriate optimization, this additional design freedom could be used to surpass the performance of the currently employed packed bed columns. Due to the increased bed homogeneity, resulting from the fact that the particles are no longer put in place by slurry-packing but are manufactured in situ by means of photolithographic etching techniques, it is especially the COMOSS approach which offers the largest potential increase in performance. Previous calculations by our group have shown that if it would be possible to produce a perfectly ordered array of porous cylindrical pillars with an external porosity of $\varepsilon = 0.4$, reduced plate heights well below unity and separation impedances as small as 200 would come within reach, respectively a factor of 2 and 10 smaller than what is currently achievable with the best possible packed beds [9]. This gain is fully due to the reduction of the *A*-term band broadening. A second potential advantage of the COMOSS concept is to be found in the possibility to move away from the typical $\varepsilon = 0.4$ porosity and round particle shape of the packed bed of spheres. This could open the road towards the achievement of even larger separation resolutions and speeds. There is however, up to now, no real theoretical basis to decide upon the optimal bed porosity and particle shape for such columns. Another problem is that the current generation of COMOSS columns [8,10] are filled with non-porous pillars, leaving the system with a very poor mass loadability and retention capacity. Columns consisting of perfectly ordered arrays of fully porous micro-pillars as discussed and schematically represented in [11] on the other hand would come very close to the ideal chromatographic system, provided they could be manufactured with a sufficient depth and with a sufficient uniformity of the flow-through pore size. Although such porous

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pillar array columns do not exist yet, we hope to contribute to the development of these systems by providing design rules for the optimal bed porosity and particle shape and by pointing at the large potential advantage of such columns.

For this purpose, we have set up a theoretical study wherein we considered a large number of different two-dimensional (2D) porous pillar arrays with varying bed porosity and particle shape and calculated their flow resistance and band broadening (under retentive conditions) over the complete range of practical velocities and characterised them by determining the van Deemter or Knox parameters. These calculations were carried out by means of a commercial computational fluid dynamics (CFD) software package (Fluent, v6.1.22), which has been extended with a number of self-written numerical routines [12,13] to simulate the diffusion and adsorption processes inside the stationary phase.

2. Considered geometries and numerical methods

In the present study, porous pillar array columns with three different pillar shapes (cylinders, ellipsoids and diamonds) and three different external porosities ($\varepsilon = 0.4$, $\varepsilon = 0.6$ and $\varepsilon = 0.8$) have been considered. The lay-out of the different pillar arrays was generated in a commercial CAD program (Gambit v2.1), starting from an equilateral triangular grid and putting a pillar centre on each grid point (Fig. 1). The reader should note that by using the same grid for all particle shapes, the number of trans-channel coupling points remains constant for all pillar shapes. This is important because, as has been pointed out in [6–14], these trans-channel coupling points are needed to overcome the excessive band broadening originating from small pore-to-pore width variations which are inevitable, even when using the best possible currently existing etching processes. We recently confirmed this on a hypothetical segmented column structure [12], showing that even a flow-through pore variability of only a few percent can already lead to a dramatic plate height increase if the number of trans-channel coupling points is too small. Given the difficulties to make any a priori assumptions on the flow-through pore variability of a real, micro-machined porous pillar array column, we therefore think it is critical for any exercise on the determination of the ideal chromatographic packing shape that the number of trans-channel coupling points remains constant. Arrays with a porosity smaller than 0.4 were not considered because such systems yield a dramatic increase of the flow resistance, and arrays with a porosity larger than 0.8 were not considered because such systems would only have a very poor zone ratio $(1 - \varepsilon)/\varepsilon$, leading to poor retention capacities and mass loadabilities.

Apart from the obvious cylindrical pillar shape, we also considered ellipsoidal and diamond-like pillars to investigate the potential advantage of a more elongated and more streamlined shape. For the ellipsoids and the diamonds, the ratio of their maximal lateral (d_{lat}) and longitudinal dimension (d_{ax}) was rather arbitrarily put at $d_{\mathrm{ax}}/d_{\mathrm{lat}} = \sqrt{3}$. Although other values certainly are possible, the $d_{\mathrm{ax}}/d_{\mathrm{lat}} = \sqrt{3}$ ratio already gives a significant elongation with respect to the cylindrical pillars, without leading to too locally constricted pore spaces (which is a problem for the ellipsoids in the $\varepsilon = 0.4$ cases [9]), or without leading to a too strong reduction of the fluid contact zone

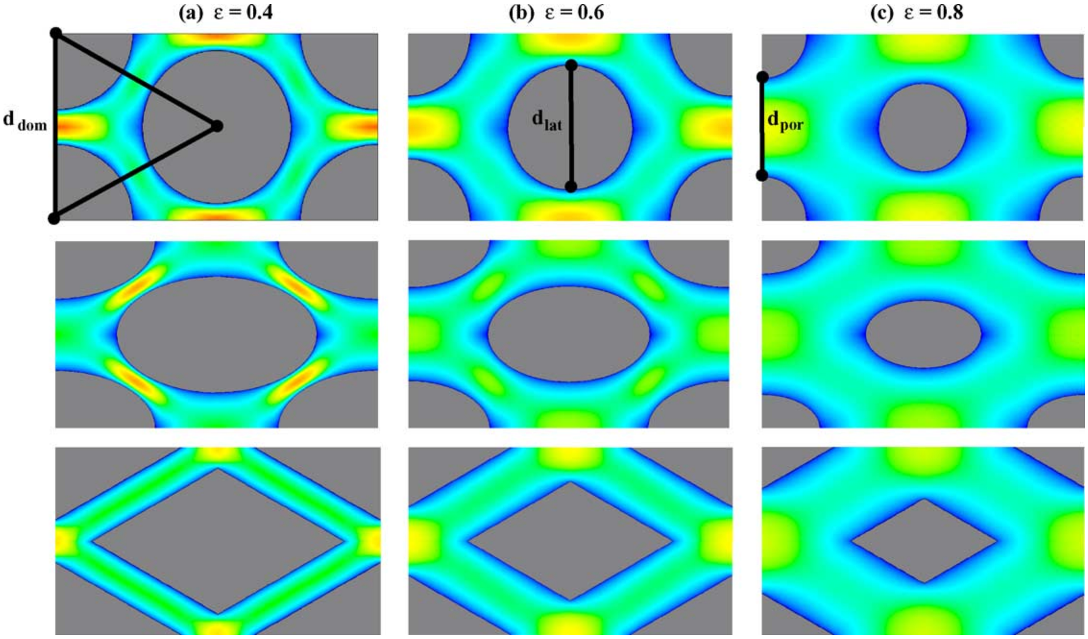

Fig. 1. Overview of the unit cells and the calculated velocity fields for the three different porosities considered pillar shapes: $\varepsilon = 0.4$ (a), $\varepsilon = 0.6$ (b) and $\varepsilon = 0.8$ (c). For each porosity, three different pillar shapes (cylinders, ellipsoids and diamonds) are considered. Represented geometries are for the constant domain size-case.