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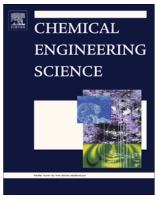

Dispersion behavior of 3D-printed columns with homogeneous microstructures comprising differing element shapes

Suhas Nawada, Simone Dimartino [1], Conan Fee *

Biomolecular Interaction Centre and Department of Chemical & Process Engineering, University of Canterbury, Private Bag 4800, Christchurch 8041, New Zealand

HIGHLIGHTS

- Columns containing ordered lattices of particles were 3D printed.
- Several particle shapes and arrangements' plate heights were measured.
- Geometrical analysis of the printed parts show good replication of CAD models.
- Tetrahedral elements achieved the lowest plate heights in a simple cubic grid.
- Face-centered cubic was found to be the optimum arrangement of spheres.

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ABSTRACT

We used additive manufacturing (3D printing) to create ordered porous beds from a range of geometric shapes, including truncated icosahedra (approximating spheres), tetrahedral, octahedral, triangular bipyramid, and stellar octangular particles. We show that the printed porous media were highly reproducible and had excellent fidelity in physically reproducing computer-aided design models, with differences between designed and experimentally measured particle locations within ±0.5%, and within 1.3% in terms of bed porosity. Experimental residence time distributions were measured and the reduced plate height, h, was determined under different reduced velocities (Peclet number, $Pe = 4–400$). The results (using equivalent particle diameter to non-dimensionalize) show that, for the simple cubic (SC) arrangement, tetrahedral particles had a lower plate height ($h_{min} = 1.56$) than all other particle shapes tested, including spherical particles. We also, for the first time, experimentally validated computational predictions of the performance of SC, body centered cubic (BCC) and face centered cubic (FCC) arrangements of spheres, confirming that FCC is indeed superior ($h_{min} = 1.12$) to SC ($h_{min} = 1.62$). We conclude that the capability offered by additive manufacturing in controlling not only packing configuration but also shape, position and orientation of the geometric elements within the porous bed may, in the future, play a fundamental role in the design of highly efficient 3D-printed columns.

1. Introduction

Randomly packed beds of spherical particles, generally created by slurry packing, have long been the predominant internal morphology for chromatographic columns. However, slurry packing continues to suffer several drawbacks such as difficulty in attaining repeatable control of the packing process, complexities in modelling and scale up of the resultant beds, and radial heterogeneities, especially near the column walls.

Ideally, random packing of a bed of monodisperse spheres results in the random close packing configuration, with an average extra-particle porosity of approximately $\varepsilon = 0.36$. Random loose packing, with $\varepsilon = 0.46$, represents the other extreme in the packing of monodisperse spheres. In industrial practice, well-packed columns traditionally have bed porosities near to the random close packing case (Guiochon, 2006), but this is usually because the particle size distribution mitigates deviations from random close packing (Billen et al., 2007; Gritti et al., 2011). Regardless, with slurry packing, one cannot design the extra-particle porosity in advance, but must accept the result of the packing procedure.

Slurry packing also inherently leads to packing heterogeneities near the column walls, where the physical boundary constrains the particle locations, producing a looser packing than in the bulk of

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* Corresponding author.
E-mail address: conan.fee@canterbury.ac.nz (C. Fee).

[1] Current address: Institute for Bioengineering, The School of Engineering, The University of Edinburgh, Edinburgh EH9 3DW, UK.

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the column. Yew et al. estimated that half of a column's potential efficiency is lost through radial heterogeneity in a packed bed (Yew et al., 2003). Furthermore, expansion and compression of the bed, as well as local movement of beads caused by varying flow rates, reduce packing quality over time, with a consequent drop in chromatographic performance (Kirkland and DeStefano, 2006). Repeatability of slurry packing is also difficult to achieve, with the exact microstructure of the bed depending heavily on a wide range of operator-dependent conditions that are virtually impossible to exactly reproduce in practice (MacNair et al., 1999).

The limited control of the final microstructures resulting from slurry packing has meant that analysis of the effects of packing geometries on column performance have tended to be empirical, *a posteriori* studies. For example, 'packing quality' is a term often used to account broadly for the fluid dispersion resulting from heterogeneities in particle shape, size and arrangement, but direct relationships of dispersion to any specific physical characteristic in the bed have not been elucidated. Analysis of chromatography performance relies on global lumped-parameter models that describe fluid dispersion using a "black box" model, while the establishment of an *a priori* fully predictive model has remained elusive (Schure and Maier, 2006).

Particle shape is another key factor determining the final packing quality. Generally, particles in packed beds have traditionally been categorized as spherical, ellipsoidal or 'irregular'. While random packing with spherical particles was found to be superior to that with irregular particles (Lottes et al., 2009), it was shown that this was due to the more homogenous morphology that spherical particles create when randomly packed.

Entirely ordered structures may offer advantages over random packing in terms of reduced fluid dispersion and improved predictability. Knox predicted a substantial increase in column performance through the use of completely homogenous structures in two dimensions (Knox, 2002). Computational results by Schure et al. later demonstrated the advantages of homogeneous beds in three dimensions, concluding that face-centered cubic (FCC) configurations of monodisperse spheres have much lower plate heights than do random close packings across a large range of reduced velocities (Schure et al., 2004). Other computational studies have given similar results (Yan and Wang, 2013; Wu et al., 2013). Wirth et al. experimentally demonstrated the advantages of a FCC arrangement of silica particles (Malkin et al., 2010; Rogers et al., 2012) but experimental studies such as this are rare because of the difficulty of producing ordered beds in practice.

The potential advantages offered by ordered configurations of particles were further investigated by De Smet et al. and Li et al., who proposed the use of ordered arrangements of particles having shapes other than traditional spheres (De Smet et al., 2004, 2005; Li et al., 2016). Their simulations predicted that axially elongated elements could improve chromatographic performance, but manufacturing limitations have made it impossible to test these shapes experimentally. The studies do however, reveal the potential of ordered lattices of non-spherical particles, if they could be manufactured reliably.

The advent of additive manufacturing, or 3D-printing, comprises a paradigm shift in our ability to physically produce complex structures that were previously practically impossible to manufacture. 3D-printing of porous beds offers the potential to create (i) completely homogeneous packing arrangements through *a priori* design, including position, orientation and alignment of the particles; (ii) radial homogeneity, in particular through printing of embedded wall features; (iii) new particle shapes that could potentially improve separation efficiency; (iv) integrated extra-column components such as inlet fittings and fluid distributors. Fee et al. demonstrated the feasibility of creating 3D-printed columns comprising ordered matrices of particles and parallel channels, within integrated columns containing flow distributors, collectors, column walls and fittings (Fee et al., 2014).

In this study, we used 3D printing to produce homogeneous porous beds. Different packing arrangement were created, for a range of different particle shapes. All columns were designed with identical bed porosities, while embedded particles were printed along the column walls to minimize wall effects. The 3D printed columns were tested experimentally to obtain plate height, flow permeability and chromatographic impedance. By minimizing packing heterogeneity and irregularities near the column walls, we were able to compare the effects of particle shape and packing configuration on the performance of the various columns.

2. Methods

2.1. Column internal morphology

2.1.1. Particle shape

We tested the effects of internal morphology, defined loosely as the "particle shape", on chromatographic performance, using spheres as a benchmark. In practice, our spherical particles were approximated by truncated icosahedra because the latter require fewer computer aided design (CAD) component planes, thus reducing computational demand on the CAD software. Initial 3D printing tests confirmed that truncated icosahedra were indistinguishable from spheres when printed at the scales used here. For convenience, truncated icosahedra are subsequently referred to herein as "spheres". The other particle shapes considered were tetrahedrons, octahedrons, triangular bipyramids (i.e. two tetrahedra adjoined at the base) and stella octangula.

A simple cubic (SC) arrangement was used to produce all the porous beds because it is the only configuration able to provide a consistent particle arrangement using all of the above particle shapes. The position, orientation and mutual alignment of the particles within the packing were held by designing partly overlapping particles. The degree of overlap was defined using an overlap factor, α, defined as follows:

$$\alpha = C_D/S \tag{1}$$

where S is the distance between the centres of neighboring particles and C_D is the circumdiameter of the particle, defined as the diameter of a sphere that circumscribes the solid shape. It is worth noting that the overlap factor is a key parameter that can be appropriately tuned to achieve specific desired properties in the porous media (Nawada et al., 2014).

The resulting internal column morphologies did not, strictly speaking, consist of discrete particles as in a conventional packed bed column, but rather were monolithic structures where the geometric elements in the SC lattice were partly truncated and connected to each other. However, the structures were much closer to ordered packings than a chromatographic monolith in the traditional sense, i.e. a porous block containing a network of randomly interconnected channels of varying shape, dimension and tortuosity. A CAD rendering of the resulting ordered porous structures is presented in Fig. 1.

The truncated particles and their resulting SC arrangements were geometrically characterized using:

- the equivalent particle diameter, D_E, defined as the diameter of an equivalent sphere having same volume as the truncated particle, V_P:

$$D_E = \left[\frac{6V_P}{\pi}\right]^{1/3} \tag{2}$$