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NUMERICAL SIMULATION ON FLOW IN COLUMN CHROMATOGRAPHY

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Monolithic columns have attracted much attention as a novel platform for high throughput analysis, but there is little information about the fluid profile in the flow channels. In this paper, we presented our approach for the fluid simulation in column chromatography by the lattice Boltzmann method (LBM). To simulate the monolithic column system, the calculation domain was modeled by the 3D channel flow through sphere obstacles. Several types of porous structure were used, with uniform and non-uniform pores. Based on the simulations results, we discussed fluid flow and pressure variation for the optimization of the suitable structure for HPLC system.

Keywords: Porous media; chromatography; numerical simulations, LBM.

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1. Introduction

Ever-increasing applications of chromatography in environmental and biological sciences require faster and more efficient columns than those traditionally available.[1] In order to achieve high sample throughput and rapid analysis, the following two approaches have been mainly pursued:[2,3,4,5] (1) the use of very fine particles with a smaller diameter and (2) the development of monolith columns. These approaches have their own advantages and disadvantages. The columns packed with sub-2 μm particles provide higher resolution and potentially higher speed compared with standard HPLC columns.[2,3] However, the cost for the improved efficiencies is higher column back-pressure, so that very high pressure pump system is required to overcome the high pressure drop generated by small particles. While, monolithic columns have attracted much attention due to their unique porous structure.[4,5]

Monolith is a single cylindrical rod having an interconnected network of flow-through channels with surface mesopores.[6] These large channels and the monolith 's specific surface result in fast mass transfer for high-resolution and fast separations. The channels also produce low back pressure, allowing the use of higher linear velocities within the pressure limitation of standard HPLC pump.[7] That is, the time required for the analysis can be shortened by simply increasing the mobile phase flow rate. However, the skeletal structure is relatively heterogeneous and the column efficiency is generally lower than that of the particle-packed column.

It is quite important to better understand these columns for any further progress in monolithic column technologies and also packing technologies. In particular, the flow of the mobile phase in the column is of great interest. However, it cannot be directly pursued by performing experiments, and thus many factors have not yet been elucidated. The present study prepared a porous material that mimicked the monolithic column and performed simulations to examine the flow field with pressure change in the monolithic column using the lattice Boltzmann method (LBM[8]).

2. Methods

The present study used a D3Q15 model to perform a three-dimensional calculation.[9] In this model, space discretization was achieved using square lattices. The flow was calculated based on the distribution function for pressure p. A porous material was prepared by arranging solid spheres in channels. Figure 1 shows the calculation domain. In this figure, the X-axis represents the flow direction, the Y-axis represents the horizontal direction, and the Z-axis represents the height direction. The porous material (the number of lattices was $101 \times 101 \times 101$) was placed at the center of the calculation domain. Since the spatial grid of δ_x was 0.35 μm, the total size of the calculation domain was X=0-56 μm, Y=0-35 μm, and Z=0-35 μm, and the porous material was placed in the range of X=10.5-45.5 μm. Table 1 shows the specifications of porous materials. The standard porous material was expressed as porous material 0, where solid spheres of 5 μm diameter were arranged so that the porous material possessed a close-packed structure. The porosity was 0.281.

The actual monolithic column is known not to possess a perfect close-packed structure. Therefore, solid spheres arranged in porous material 0 with a close-packed structure were removed from it to prepare other porous materials that mimicked the monolithic column. When the solid spheres were regularly removed from porous material 0, the porous material was named porous material 1. When irregularly removed, the porous material was named porous material 2 (6 types of 2A-2F). In order to prepare various monolithic columns with different internal structures, the number of solid spheres to be removed was changed. Consequently, the porosity ε and the flow characteristics varied. The boundary conditions were as follows: (1) an inflow boundary was adopted for the inlet; (2) a symmetric plane was set for the top, bottom, right, and left walls; and (3) a free outflow boundary was adopted for the outlet. A standard bounce-back condition of non-slip boundary was imposed on the sphere surface. Water was used as the fluid, and the flow rate was either 1 or 10 mm/s.

3. Results and Discussion

3.1. *Porosity and Flow Field*

Figure 2 shows the porosity distributions of porous materials 0, 1, and 2A. The value in this figure was the average on the YZ-plane. The porosity of porous mate-

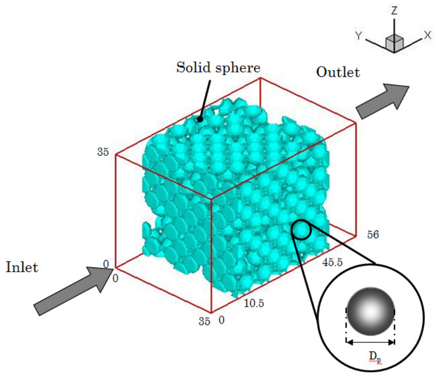

Fig. 1. Numerical domain and porous material 2A.

rial 0 periodically varied in a range between 0.26 and 0.35. This periodic variation was due to the regular arrangement of solid spheres. The average porosity was 0.28, which exhibited a close-packed structure. In porous material 1, which was obtained by regularly removing solid spheres from porous material 0, the average porosity periodically varied. In porous material 2A, which was obtained by irregularly removing solid spheres from porous material 0, the porosity randomly varied. The average porosity of porous material 1 was 0.468, and that of porous material 2A was 0.470; these values were similar to each other.

Figure 3 shows the flow field on the XY-plane of porous material 1 at Z=0 μm and the XY-plane of porous material 2 at Z=7 μm. The flow rate was 1 mm/s. Although the regular flow passing through voids between solid spheres was observed in porous material 1, the flow was concentrated at a region in porous material 2 where many solid spheres had been removed.

Table 1. Porous material.

NO	Type	ε	δ_x (μm)
0	-	0.281	0.35
1	regular	0.468	0.35
2A	random	0.470	0.35
2B	random	0.467	0.35
2C	random	0.471	0.35
2D	random	0.471	0.35
2E	random	0.470	0.35
2F	random	0.467	0.35

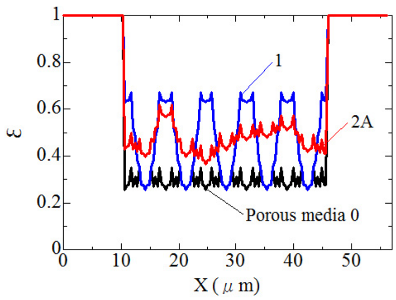

Fig. 2. Averaged porosity in YZ-plane.

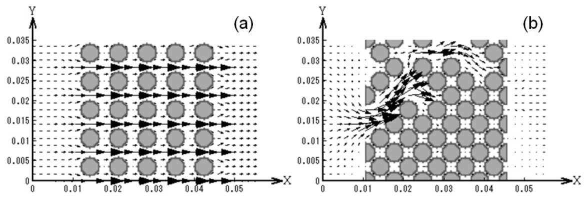

Fig. 3. Flow field in XY-plane; (a) porous material 1, (b) porous material 2A.

3.2. *Pressure Field and Comparison with the Ergun Equation*

Figure 4 shows the pressure distributions of porous materials 0, 1, and 2A in the flow direction. In this figure, the flow rate was 1 mm/s, and the value was the average on the YZ-plane. As shown in this figure, the pressure gradient in the monolithic column was almost constant in all materials. When porous materials 0, 1, and 2A were compared, the inlet pressure decreased by removing solid spheres from porous material 0 with a close-packed structure (i.e., water easily flowed in porous materials 1 and 2A). When porous materials 1 and 2A were compared, the inlet pressure was smaller in porous material 1 from which solid spheres had been regularly removed. Therefore, the inlet pressure differed depending on the manner of removing solid spheres. The change in pressure due to different flow rates was investigated. Consequently, when the flow rate was changed from 1 mm/s to 10 mm/s (10 times), the difference in pressure before and after the monolithic column (pressure loss) was approximately 10 times.

Next, the validity of the simulation results was verified. Using three porous materials 0, 1, and 2A, the friction factor f in the channel at a fixed flow rate of 1 mm/s was obtained. In reality, the flow velocity in the liquid chromatography is 1 mm/s,[1] and the flow rate was set to be 1 mm/s. Subsequently, the obtained coefficient was compared with a result obtained using the Ergun equation of $f =$

150/Re + 1.75,[10] where Re is a Reynolds number. This well-known formula is an empirical equation for porous media flow. Figure 5 shows the comparison results. It is found that simulation results almost agreed with the Ergun equation. Therefore, in porous materials 1 and 2A that mimicked the monolithic column, the flow in porous media was reproduced.

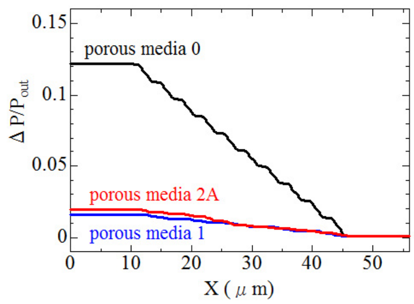

Fig. 4. Averaged pressure in YZ-plane.

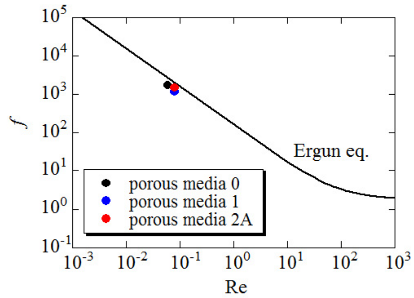

Fig. 5. Variations of friction factor with Re.

3.3. *Pressure Field in Porous Material 2*

Based on the results shown in Fig. 4, the inlet pressure was smaller in porous material 1, from which solid spheres had been regularly removed. However, since only one porous material 2A, from which solid spheres had been irregularly removed, was examined, different manners of removing solid spheres from porous material 0 could have resulted in different outcomes. Therefore, more simulations were conducted using the porous materials 2B-2F. Figure 6 shows the flow fields of porous materials 2B and 2C on the XY-plane at Z=7 μm as examples. In this figure, the flow rate was 1 mm/s. Although the flow fields of porous materials 2B and 2C clearly differed from those of porous material 2A (shown in Fig. 3b), these three porous materials exhibited the same tendency that the flow was concentrated at a region where many solid spheres had been removed.

Finally, the pressure distribution was compared among porous materials 2A-2F. Figure 7 shows the comparison results. In this figure, the flow rate was 1 mm/s. As shown in this figure, the pressure change was similar among these porous materials. When the pressure distributions were compared with that of porous material 1 (shown in Fig. 4), the inlet pressure of porous material 1, from which solid spheres had been regularly removed, was always smaller than those of porous materials 2A-2F. Therefore, it was suggested that the use of a porous material with a uniform porosity could reduce the pressure in the column.

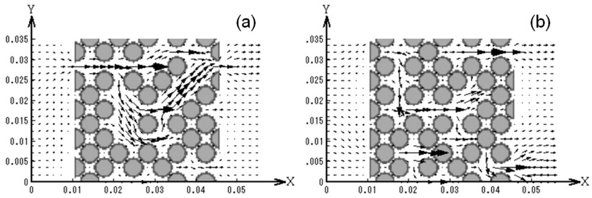

Fig. 6. Flow field in XY-plane; (a) porous material 2B, (b) porous material 2C.

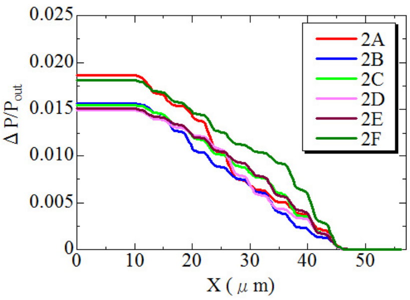

Fig. 7. Averaged pressure in YZ-plane.

4. Conclusion

The present study prepared a porous material that mimicked the monolithic column and performed simulations on flow field using the LBM. The friction factor obtained by the simulation was similar to the value estimated using the Ergun equation. Even though the average porosity was the same, the flow and the pressure differed, depending on the arrangement of solid spheres. The inlet pressure was smaller in porous material where solid spheres were regularly arranged than in those where solid spheres were irregularly arranged. In the future, we will prepare porous materials whose properties are approximate to those of the monolithic column for optimization of skeletal structure and size of the monolithic column.

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