Korean J. Chem. Eng., 33(12), 3337-3342 (2016)
DOI: 10.1007/s11814-016-0286-0

pISSN: 0256-1115
eISSN: 1975-7220

RAPID COMMUNICATION

Minimizing axial dispersion in narrow packed column using superhydrophobic wall

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(*Received 30 July 2016 • accepted 11 October 2016*)

Abstract−The scope of minimizing dispersion in narrow packed column using superhydrophobic (SH) wall is assessed experimentally with implications in analytical techniques such as liquid chromatography. The study includes devising a packed column (7-19 mm) with lotus leaf pasted on the inner wall and establishing a gravity driven flow through it. The flow dispersion is characterized based on the residence time distribution study of the column. The results are compared against similar flow through smooth packed column. Experimental results reveal the influence of two factors: column diameter as well as the wall features, superhydrophobic or smooth. For similar surface features, the axial dispersion reduces with decrease in column diameter due to the increase in voidage, which leads to plug flow. For the same diameter, between smooth and superhydrophobic, effects of slip in the latter reduce the dispersion significantly. Thus, the introduction of superhydrophobic narrow columns can play a crucial role in minimizing dispersion in analytical techniques.

Keywords: Axial Dispersion, Narrow Packed Column, Superhydrophobic Wall, Residence Time Distribution, Slip

INTRODUCTION

Axial dispersion affects the performance in several analytical techniques, including liquid chromatography by reducing the resolution of species to be separated [1]. Therefore, minimizing dispersion in such techniques is key to improved sensitivity in detection [2-4]. Methods to minimize dispersion include tailoring flow by modifying flow cross section and actuation methods [5-8]. Scope for newer methods for manipulating flow exists such as by modifying wall effects. Dedicated research in this area is necessary for improving the analytical techniques.

The key flow characteristic affecting dispersion is the velocity variation along the cross section. Dispersion is minimum for plug flow and increases with increase in the variation [9]. Intuitively, dispersion decreases with increase in Reynolds number as flow assumes more and more plug-like shape from parabolic. Plug flow occurs because of slip at the wall brought in by flow mechanisms such as electroosmotic flow (EOF), which is based on electrostatic interaction of electrical double layer (EDL) with external electric field. EOF has been employed in capillary electrochromatography (CEC) [1,10,11]. Notably, they exhibit much reduced dispersion as compared to pressure driven flow in high performance liquid chromatography (HPLC) [12].

Alternative method of inducing slip by surface modifications at wall exists. This includes the use of superhydrophobic (SH) walls [13,14] particularly in narrow packed columns where flow is highly confined. SH surface is characterized by periodic microstructures of gaps and pillars (~10 μm) [15,16]. When submerged, the gaps trap air generating an air liquid interface. The interface allows slip during flow that minimizes drag drastically [17-21]. A correlation of slip length with the drag reduction has been established previously [22,23].

Despite much focus on drag reduction, studies on dispersion over SH surface are relatively few. This includes theoretical modeling of dispersion in presence of a constant slip length [24-26] and numerical simulations on an SH lotus leaf cylindrical channel [27]. The studies predict a reduced dispersion for a wide range of Peclet number (Pe) and highlight the role of slip in minimizing dispersion. However, the finding requires proper experimental validation. Due to the relevance of dispersion in liquid chromatography, the concept ideally needs to be explored in narrow packed column.

Our objective was to explore the scope of reduced dispersion in narrow packed column. The study includes devising a test column by layering lotus leaf on the inner wall and passing gravity driven flow through it. The flow dispersion is characterized based on the residence time distribution study of the column. The results are compared against similar flow through smooth column. The dispersion number is evaluated. The dependence on column diameter (D) and wall features is analyzed.

EXPERIMENTAL

SH column was fabricated by using flat flexible transparent sheets (thickness-100 μm, Fig. 1). The fabrication technique involved coating the sheets with lotus leaf and then rolling it into cylindrical column of desired diameter (7 mm, 10 mm, 15 mm, 17 mm and 19 mm). The column diameter range was considerably low (7-19 mm), which maintained close proximity of walls. Typical height of column was fixed at 145 mm. Spherical steel balls of diameter D_p= 3.6 mm (D/D_p~1.9-5.2, ρ_s=7,900 kg/m^3) were used as packing material and packing height was kept at 105 mm. The fabricated columns were stacked on a base of molten wax kept in a glass crucible which was allowed to solidify. An outlet was provided on the side

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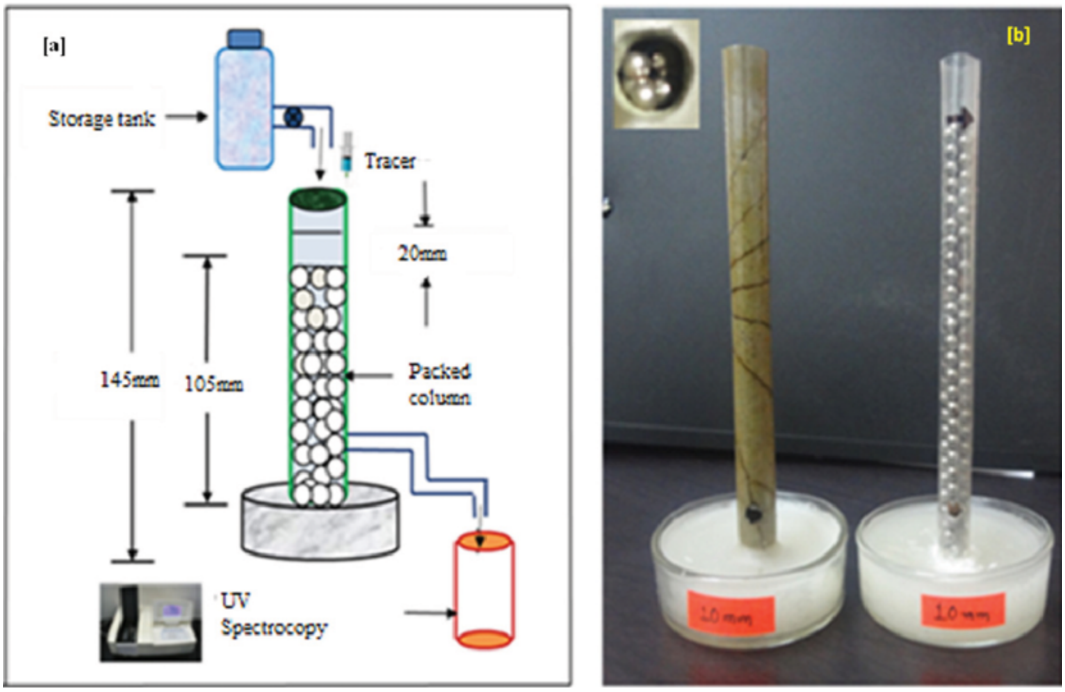

Fig. 1. Set up (a): Schematic (b): Smooth and superhydrophobic column fabricated using lotus leaf. Contact angle over lotus leaf is 157° compared to 57° over transparent sheet.

Table 1. Summary of flow features

D, mm	D/D_p	Φ	Volumetric flow rate $m^3/sec\times10^{-6}$		Superficial velocity m/sec		Particle Reynolds number, Re_p	
			Smooth	SH	Smooth	SH	Smooth	SH
19	5.28	0.33	7.65	8.30	0.027	0.030	162	176
17	4.72	0.37	7.08	7.83	0.031	0.034	201	222
15	4.17	0.43	7.06	7.26	0.040	0.041	283	290
10	2.17	0.55	4.08	4.71	0.052	0.060	473	547
7	1.94	0.65	2.52	2.70	0.065	0.073	750	841

at the bottom. During each run, liquid was constantly fed from a reservoir to keep the packing material submerged, thereby ensuring a gravity-driven steady flow through the porous media. The flow rate at the outlet was measured. For residence time distribution (RTD) study, tracer of 50 ppm methylene blue solution was injected as a pulse input to the liquid layer over the column packing. The exit liquid concentration was analyzed with a spectrophotometer (Thermoscientific Fischer Evolution 300). Experiments were conducted for packed column using plain water. For each run, mass flow rate was measured and RTD was obtained. Non-dimensional variance σ_θ was obtained as σ^2/t_m^2 where σ is the variance and t_m is the mean residence time.

$$\sigma_\theta^2=\frac{1}{t_m^2}\int_0^\infty(t-t_m)^2E(t)dt \quad (1)$$

The dispersion number, D/uL is calculated by substituting value of σ_θ in variance relation for closed-closed vessel configuration [28]

$$\sigma_\theta^2=2\frac{D}{uL}-2\left(\frac{D}{uL}\right)^2[1-e^{-uL/D}] \quad (2)$$

Repeatability of RTD runs lies within 2.2% for smooth column and 3.5% for SH column, which is well below the variation in the trends for the different columns and wall features.

RESULTS AND DISCUSSION

1. Flow Characteristics

Table 1 summarizes the flow features including measured flow rate, superficial velocity, $Re_p=(D_p v_s \rho/(\mu(1-\phi))$ for smooth and superhydrophobic column, where Re_p is the particle Reynolds number, v_s is superficial velocity of the flowing liquid, μ is viscosity of flowing liquid and φ is void space. Re_p lies in the turbulent regime >>10. In both cases, Re_p varies with D/D_p for slender columns: increases with decrease in diameter. This can be explained based on the effect of void fraction on the flow. For lower D/D_p, the φ is high because the interstitial pockets allow bulk passage of liquid. With increase in D/D_p, the voidage decreases, which brings the packing-walls closer to each other and enhances the viscous effects. Fig. 2(a) plots the Re_p vs the non-dimensional column diameter for smooth as well as SH columns. The Re_p drops asymptotically, sat-

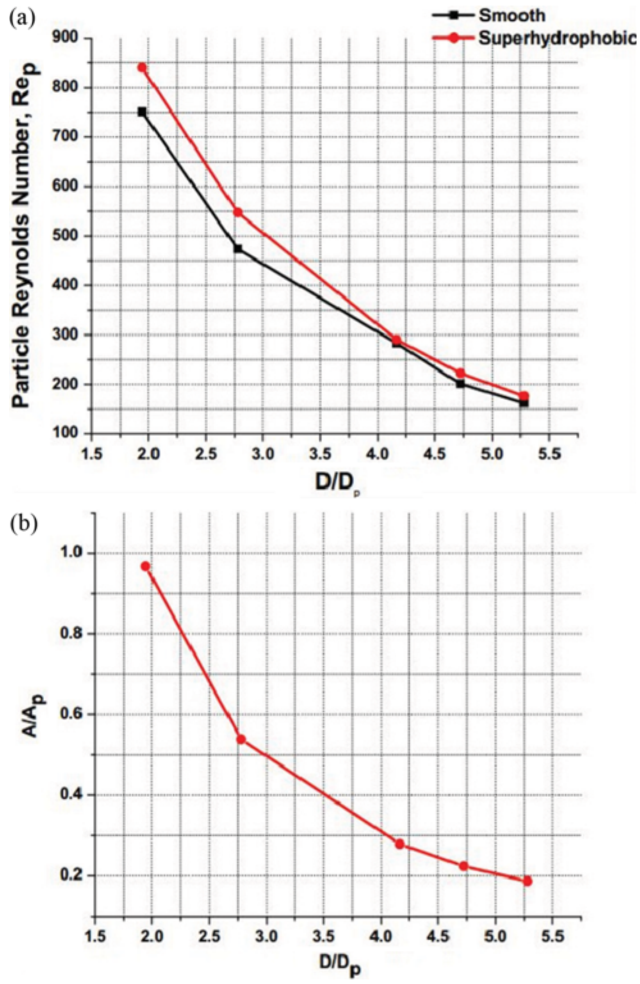

Fig. 2. (a) Particle Reynolds number varying with non-dimensional diameter due to effects of void faction. Curve for SH column higher for effects of flow slippage. (b) Relative surface area A/A_p varying with non-dimensional diameter due to effects of void fraction.

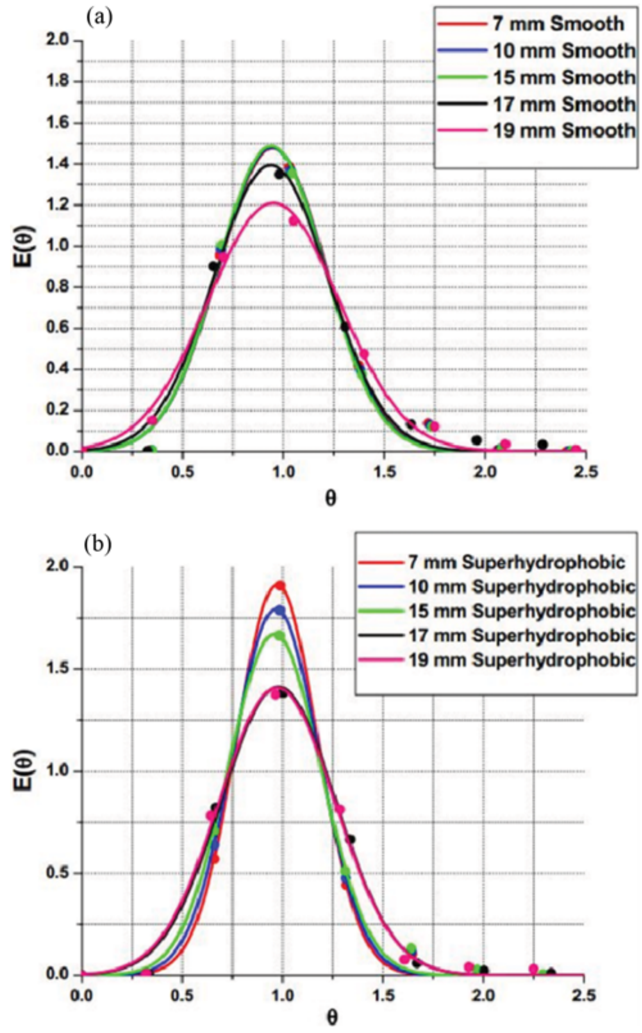

Fig. 3. Exit age concentration distribution (a): Smooth column (b): SH column. Colored dotted marks represent experimental values. Dashed lines represent Gaussian fit which is an approximation for the given Pe number range.

urating beyond D/D_p~5, restricting the influence of diameter ratio further. The Re_p values for SH surface are higher than that of smooth, suggesting a role of enhanced flow slippage at the wall. The difference increases with increasing effect of slippage for the increasing Re_p. The effects of enhanced slippage can be further explained based on the surface area ratio of wall and packing: $(A/A_p)=(2D_p/3(1-\phi)D)$ (Appendix) which is plotted as function of D/D_p in Fig. 2(b), where A is surface area of wall exposed and A_p is area of particles. The value of A/A_p increases with decrease in D/D_p For example at D/D_p of 1.9, the A/A_p ratio is 0.967 while at D/D_p of 5.2 it is 0.18. Therefore, effects of SH wall dominate at low D/D_p when voidage is more (liquid encounters more contact with superhydrophobic wall to particle wall). Thus, the flow through narrow SH packed column is influenced by effects of voidage and also slip effects at the wall.

2. Exit Age Distribution E(θ)

The effect of flow on the exit age concentration is analyzed through RTD studies of the column for the different diameters. Analysis includes addressing the effects of diameter and slippage separately (Fig. 3). In the first case, we considered independent plots of RTD distribution in smooth and SH column for the different diameters. The normalized distribution gets leaner with decrease in column diameter for both (area under curve is 1). This can be interpreted based on the earlier trends of Re_p variation with column diameter. A higher Re_p at lower diameter indicates a more turbulent flow and a flatter profile leading to lesser dispersion. Contrarily, lesser Re_p at higher diameter implies tendency towards laminar regime or a relatively non-uniform flow profile due to viscosity effects of the wall. The effects of slippage are analyzed by one-to-one comparison of RTD plots for same column diameter (Fig. 4). Since the effect of voidage remains the same for a given radius, flow differs only because of slippage at the wall. Due to enhanced flow slippage at the SH wall, Re_p is high and leads to lesser dispersion. When we compare among the plots, the effects are maximum at the lowest diameter. The trends agree with the most favorable flow condition of increased voidage (increased A/A_p) and enhanced slippage.

3. Axial Dispersion

The column dispersion number is calculated using Eq. (2) and

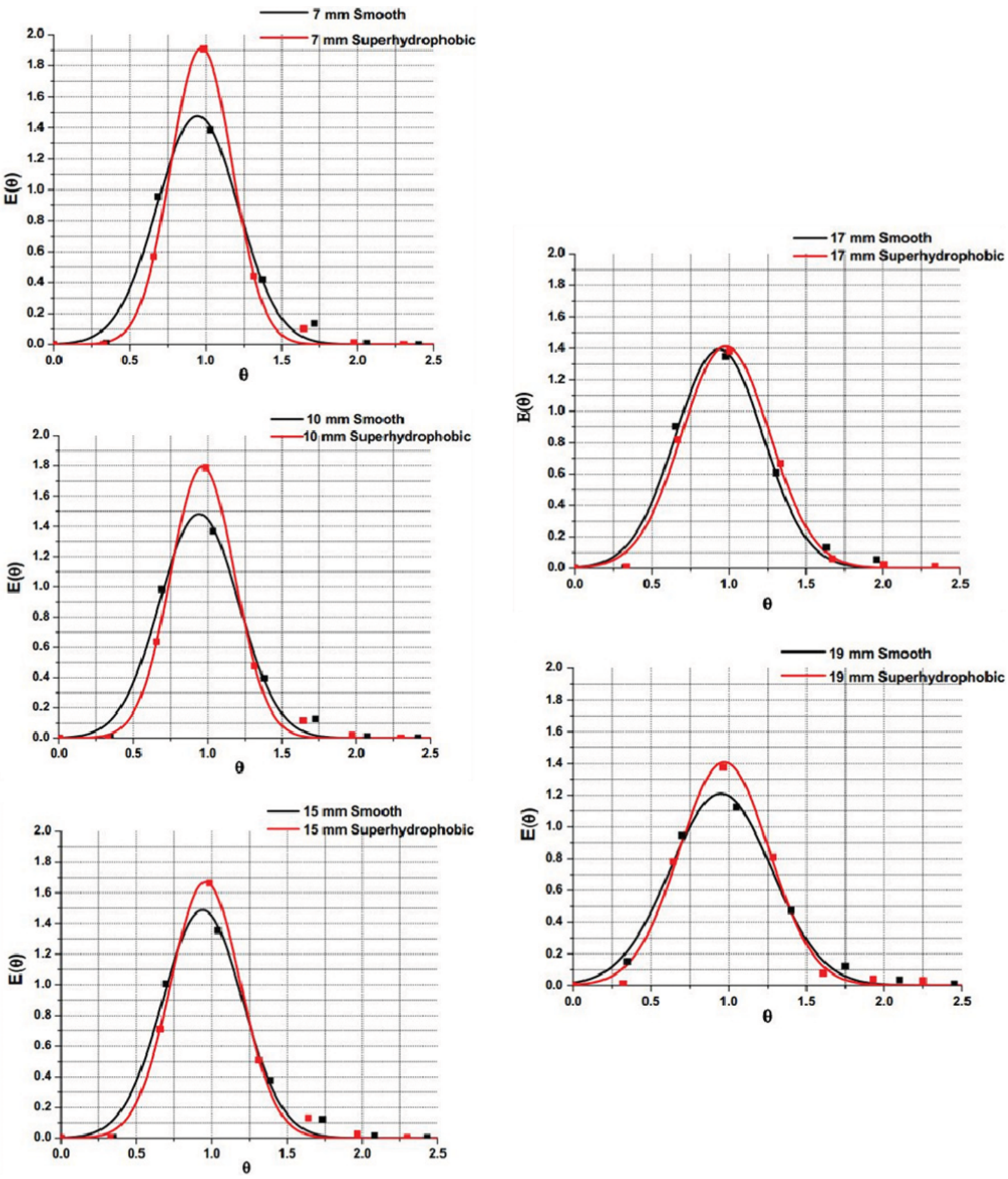

Fig. 4. Comparison of RTD for smooth and SH column.

plotted in Fig. 5(a) along with axial dispersion coefficient. The column dispersion number decreases with decrease in diameter. This is an obvious outcome of the sharper distribution curves and only highlights the non-uniform flow at higher diameter as compared to lower ones. Pe is directly proportional to Re_p. Between smooth and SH column, the dispersion number for SH surface is still lower, once again an outcome of flow slippage. The range of Pe lies within 17-30 for smooth and 25-37 for SH column. The range of Pe corresponds to the intermediate zone. These results are promising, and more enhanced effects may occur if the scale of column is further lowered. Axial dispersion coefficients for all the column diameter were calculated directly from the column dispersion

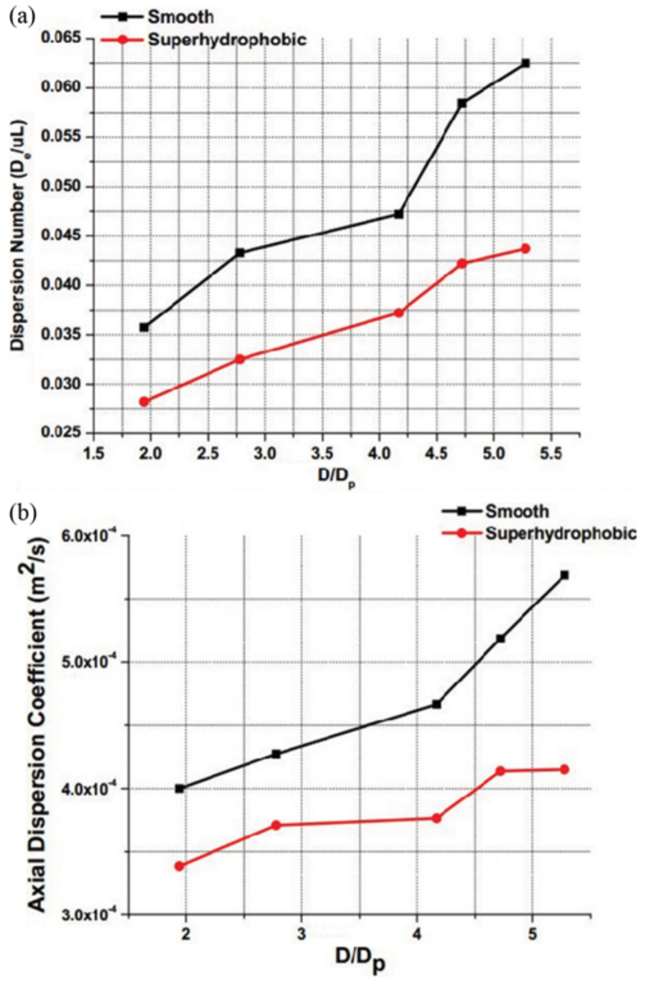

Fig. 5. Variation of (a): Dispersion number (b): Column Peclet number with D/D_p for smooth and SH surface.

number and are plotted in Fig. 5(b). Similar trends as for dispersion number are observed. Lowering the diameter leads to lower axial dispersion coefficient irrespective of smooth or SH wall. This occurs even when the superficial velocities are relatively higher at lower diameters. It implies that the plug-like nature of flow is more dominating that its magnitude. For a smooth column, the values lie from 40×10^{-5}-56×10^{-5} m^2/s. For the same diameter, the axial dispersion coefficient is found to be lower for the SH layered columns. The values lie in the range from 33×10^{-5}-41×10^{-5} m^2/s.

CONCLUSION

The axial dispersion in narrow packed column using superhydrophobic (SH) wall is investigated based on residence time ditribution studies for smooth and SH column of different diameter under turbulent flow conditions. It is observed that increased voidage in lower diameter columns leads to higher Re_p and Pe, which results in sharper exit-age distribution curve. For a given diameter, the addition of SH walls generates sharper curves. Thus, experimental results establish the influence of two factors on the RTD curves: column diameter and wall features. Dispersion number lies between 0.035-0.07 for smooth and 0.03-0.045 for SH column. The values reduce with decrease in column diameter. The results are highly promising for minimizing dispersion in anlaytical techniques by using microfabricated superhydrophobic columns.

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APPENDIX

$$\frac{A}{A_p} = \frac{\pi DL}{n \times \frac{\pi D_p^2}{4}} = \frac{DL}{nD_p^2} \tag{1}$$

Where: A: surface area of wall
A_p: total surface area of particles
D: diameter of column
R: radius of column
D_p: diameter of particle=3.6 mm
R_p: radius of particle
L: length of packed bed=105 mm
n: number of particles.
n=Volume of all particles/Volume of 1 particle
Volume of all particles=Volume of Column−Volume of void space

$$n = \frac{V_c - \phi V_c}{V_p}$$

$$\therefore n = \frac{\pi R^2 L(1-\phi)}{\frac{4}{3}\pi R_p^3} = \frac{3L(1-\phi)D^2}{2D_p^3} \tag{2}$$

V_c: volume of column
V_p: volume of 1 particle
Φ: void fraction

Substituting value of n in (1) we get:

$$\frac{A}{A_p} = \frac{2D_p}{3D(1-\phi)}$$