ANOTHER LOOK AT THE COLLOID PARTICLE SIZE-DEPENDENT DISPERSIVITY

CHRYSIKOPOULOS C.V.[1] and KATZOURAKIS V.E.[2]

[1]School of Environmental Engineering, Technical University of Crete, 73100 Chania, Greece, [2] Organization Department of Civil Engineering, Environmental Engineering Laboratory, University of Patras, Patras 26500. Greece
E-mail: cvc@enveng.tuc.gr

ABSTRACT

Accurate prediction of contaminant and colloid transport in porous media relies heavily on usage of suitable dispersion coefficients. The widespread procedure for dispersion coefficient determination consists of conducting tracer experiments and subsequently fitting the collected breakthrough data with an advection-dispersion transport model. The fitted dispersion coefficient is assumed to characterize the porous medium and is often used thereafter to analyze experimental results obtained from the same porous medium with other solutes and colloids. The above-described procedure inherently assumes that the dispersive flux of all solutes and colloids under the same flow field conditions is exactly the same. Consequently, this procedure should be avoided.

In this study an extensive laboratory study was undertaken to assess whether the dispersivity, which traditionally has been considered to be a property of the porous medium, is dependent on colloid particle size and interstitial velocity. A total of 48 colloid transport experiments were performed in columns packed with glass beads under chemically unfavorable colloid attachment conditions. Nine different colloid diameters, and various flow velocities were examined. The breakthrough curves were successfully simulated with a mathematical model describing colloid transport in homogeneous, water saturated porous media. The experimental data set collected in this study demonstrated that the dispersivity is positively correlated with colloid particle size, and increases with increasing velocity.

Keywords: dispersivity, colloids, saturated porous media, colloid transport, particle size, packed column, colloid retention.

1. Introduction

Numerous laboratory- and field-scale studies have focused on estimation of either the longitudinal dispersion coefficient (Han *et al.*, 1985, Chrysikopoulos *et al.*, 1990; Delgado, 2006), or the transverse dispersion coefficient (Delgado and Guedes de Carvalho, 2000; Olsson and Grathwohl, 2007). Transverse dispersion is increasingly recognized as a controlling mass transfer mechanism for contaminant plume migration and NAPL dissolution in aquifers (Chrysikopoulos *et al*., 2003; Rahman *et al.*, 2005; Acharya *et al.*, 2007). Hydrodynamic dispersion coefficients are strongly dependent on interstitial fluid motion and molecular diffusion. Transverse dispersion coefficients are considerably smaller than longitudinal dispersion coefficients. Numerous correlations, which are typically derived from experimental observations, are available for the estimation of hydrodynamic dispersion coefficients for solute transport in porous media (Delgado, 2006).

Previous studies have suggested that colloid transport in porous media is significantly affected by particle size (Fontes *et al.*, 1991, Gannon *et al*., 1991). Early breakthrough of colloids and biocolloids as compared to that of conservative tracers has been observed in several studies (Dong *et al.*, 2002; Keller *et al.*, 2004; Sinton *et al.*, 2012). Colloid early breakthrough can be attributed to volume size exclusion, preferential flow paths through high conductivity regions, and exclusion from the lower velocity regions (Chrysikopoulos and Abdel-Salam, 1997; Dong *et al.*, 2002; Ahfir *et al.*, 2009), which can also be viewed as a reduction of the effective porosity of

the porous medium (Morley *et al.*, 1998). The finite size of a colloid particle excludes it from the slowest moving portion of the parabolic velocity profile within a fracture or a pore throat, thus the effective particle velocity is increased, while the overall particle dispersion is reduced compared to Taylor dispersion, but with a tendency to increase with increasing particle size over a certain range of particle diameters (James and Chrysikopoulos, 2003).

This study evaluates the influence of colloid particle size on dispersivity. A large number of colloid transport experiments were performed in columns packed with glass beads. The experimental breakthrough data were fitted with an analytical colloid transport model.

2. Mathematical model description

There are numerous mathematical models available that describe colloid transport in porous media. These models rely on either continuum or statistical approaches. Continuum approaches are based on macroscopically derived conservation equations and do not consider the morphology of the pore space within the solid matrix. Continuum approaches are divided into two groups: (a) phenomenological models, which make use of several parameters that may not be possible to estimate independently due to insufficient experimental data, and (b) trajectory based models, which use force balances to compute the actual paths of the colloids in the pore space. Statistical approaches account for the morphology of the pore space, and thus require relatively large computational power. The statistical approaches are divided into two groups: (a) random processes (Markov processes) or queueing theory (birth-death processes), and (b) network models. In this study, the frequently employed continuum approach was adopted (Chrysikopoulos and Syngouna, 2014). The transport of colloids (including biocolloids) in one-dimensional, homogeneous, water-saturated porous media with first-order attachment and inactivation is governed by the following partial differential equation (Sim and Chrysikopoulos, 1995):

$$\frac{\partial C(t,x)}{\partial t}+\frac{\rho_b}{\theta}\frac{\partial C^*(t,x)}{\partial t}=D_L\frac{\partial^2 C(t,x)}{\partial x^2}-U\frac{\partial C(t,x)}{\partial x}-\lambda C(t,x)-\lambda^*\frac{\rho_b}{\theta}C^*(t,x) \qquad (1)$$

where C [M/L^3] is the concentration of colloids in suspension; C* [M/M] is the concentration of colloids attached on the solid matrix; t [t] is time; U [L/t] is the interstitial velocity; ρ_b [M/L^3] is the dry bulk density of the solid matrix; λ [1/t] is the transformation rate constant of colloids in solution; λ^* [1/t] is the transformation rate constant of attached colloids; and D_L [L^2/t] is longitudinal hydrodynamic dispersion coefficient:

$$D_L=\alpha_L U+\mathcal{D}_e \qquad (2)$$

where α_L [L] is the longitudinal dispersivity; And D_e [L^2/t] is the effective molecular diffusion. The rte of colloid attachment onto the solid matrix is assumed to follow a first-order equation (Sim and Chrysikopoulos, 1995). For a semi-infinite one-dimensional porous medium in the presence of a colloid source in the form of an “instantaneous” pulse, the appropriate initial and boundary conditions are:

$$C(0,x)=0 \qquad (3)$$

$$-D_L\frac{\partial C(t,0)}{\partial x}+UC(t,0)=M_\delta\delta(t) \qquad (4)$$

$$\frac{\partial C(t,\infty)}{\partial x}=0 \qquad (5)$$

where M_δ is the mass injected “instantaneously” over the cross-sectional area of the column. The analytical solution to equations (1) subject to conditions (3)-(5) can be found in the work published by Thomas and Chrysikopoulos (2007).

3. Experimental procedures

3.1. Colloids

In this study, fluorescent polysterene microspheres with diameters d_p=28, 300, 600, 1000, 1750, 2100, 3000, 5000, and 5500 nm were used as model colloid particles. Microsphere concentrations were measured by a fluorescence spectrophotometer (Cary Eclipse, Varian, Inc.). Each effluent colloid concentration was measured three times. Note that microspheres are sensitive to removal mechanisms such as straining (particle trapping in pore throats that are too small to allow particle passage) and wedging (particle attachment onto surfaces of two or more collector grains in contact). However, straining and wedging are not considered important mechanisms of mass loss in the packed columns examined in this study, because the colloid to collector diameter ratios (d_p/d_c) were well below the suggested threshold of 0.003 (Bradford and Bettahar, 2006) for all cases examined. The colloids were inserted at the entrance of the column with a syringe (1-2 mL) in the form of an “instantaneous” pulse injection.

3.2. Packed columns

Colloid transport experiments were conducted in glass columns with diameter 2.5 cm and length L=15 or 30 cm, packed with spherical glass beads with diameter d_c=2 mm. Each column was packed with glass beads under standing distilled deionized water For each column the dry bulk density (1.60–1.64 g/cm^3) and porosity (0.39–0.43) were determined. The columns were placed horizontally to minimize gravity effects (Chrysikopoulos and Syngouna, 2014). A fresh column was packed for each experiment.

Several water flow rates, Q [L^3/t], ranging from 1 to 6 mL/min were employed in this study. All experiments were conducted under chemically unfavorable colloid attachment conditions (pH=7, I_s=0.1 mM). Effluent samples were collected on pre-selected time intervals. Sample analysis was carried out immediately after the completion of each experiment. Finally, for each colloid breakthrough data set collected, the nonlinear least squares regression package ColloidFit was used to estimate the unknown model parameters.

4. Results

For each colloid transport experiment conducted in this study, the fitted parameters U and D_L were used for the determination of the corresponding longitudinal dispersivity. The relationship between dispersivity and colloid particle size is explored by plotting in Figure 1 all of the longitudinal dispersivity values determined in this study against colloid diameter.

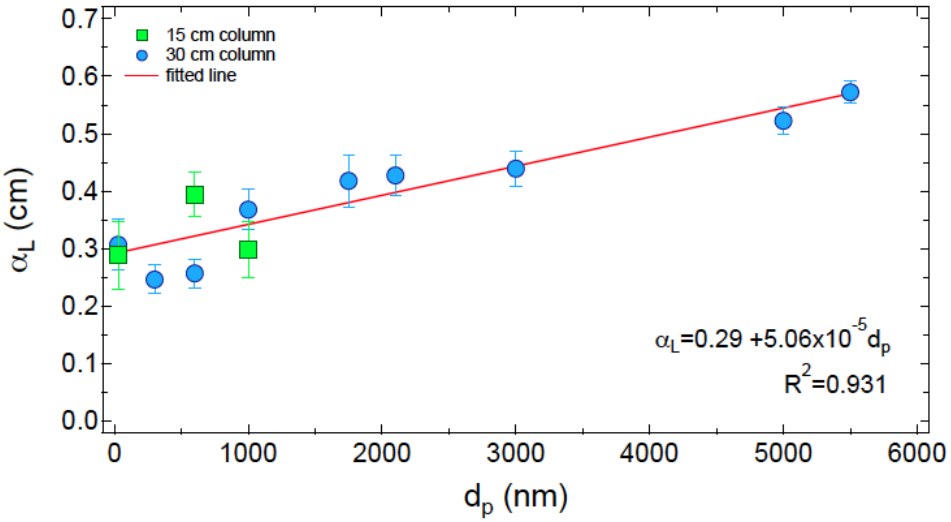

Figure 1: Averaged longitudinal dispersivity as a function of colloid particle diameter. The symbols represent the experimental data, and the solid line is a standard linear regression line.

Clearly, it is evident from Figure 1 that there is an obvious trend of dispersivity with increasing colloid particle diameter. Clearly, there is a positive correlation between α_L and d_p, which is of the form:

$$\alpha_L\left[\text{cm}\right] = 0.29+5.06\times10^{-5}\ d_p\left[\text{nm}\right] \quad (6)$$

Note that the preceding correlation predicts the longitudinal dispersivity in cm, and the colloid diameter should be in units on nm.

The observed increase in α_L is attributed to size exclusion, possible existence of preferential flow paths, and exclusion from the lower velocity regions. Thus, some colloids are getting slowed down having to pass through small pore spaces, where other colloids are managing to stay in fast flow paths.

5. Conclusions

This experimental work has shown that colloid dispersivity is not only a function of scale, as conventionally assumed, but also a function of colloid diameter. It was shown that dispersivity increases linearly with increasing colloid particle size. This phenomenon was attributed to colloid dispersion enhancement due to possible reduction of the effective porosity, and by colloid exclusion from the lower velocity regions.

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