Solute Transport in Sand Columns as Affected by Effluent Surface Tension

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Abstract: Transport of nonreactive solutes in soils is principally controlled by soil properties, such as particle-size distribution and pore geometry. Surface tension of soil water yields capillary forces that bind the water in the soil pores. Changes in soil water surface tension by contaminants may affect flow of soil water due to decreased capillary forces, caused by lowered soil water surface tension. This study aimed at assessing solute transport in sand columns as affected by effluent surface tension. Miscible displacement (MD) tests were conducted on sand columns repacked with sands sieved from 2.0, 1.0, 0.5 and 0.25 mm screens. The MD tests were conducted with 0.05 M bromide solutions prepared using water with surface tension adjusted to 72.8, 64, 53.5 and 42 dyne/cm². Obtained breakthrough curves were modeled with the convection-dispersion equation (CDE) model. Coefficient of hydrodynamic dispersion and pore-water velocity responded inconsistently across decreased particle-sizes and water surface tensions and this was attributed to non-uniform effect of lowered effluent surface tension on solute transport in different pore-size distribution.

Key words: Breakthrough curve, hydrodynamic dispersion, convection dispersion equation, pore-water velocity, miscible displacement.

1. Introduction

Contamination of groundwater and surface water systems by industrial, municipal and agricultural chemicals has focused considerable attention on solute transport in soils [1]. Solute transport in a porous medium is controlled by properties of the porous medium and solutes. Pore geometry is the primary soil characteristic that control solute transport [2]. Interaction between transported solute and particle surfaces has a strong control on transport and retention of solutes in soils [3].

Many models have been developed to describe transport of water and solutes through porous media [3]. Convection-dispersion equation (CDE) model is one of the most commonly used models [4]. The CDE model is widely used in modeling breakthrough curves (BTCs) of solutes from disturbed and undisturbed soils [5, 6]. The CDE can account for

hydrodynamic dispersion, advection and retardation of the solutes. The widespread use of CDE models in interpreting chemical transport phenomena in natural porous media is well documented elsewhere [7].

Miscible displacement (MD) tests have long been used to evaluate the solute transport characteristics of porous media [8-12] and many others. The MD tests can lead to an understanding of the physical, chemical and microbiological processes that control solute dispersion, convection and retardation in soils [13, 14]. MD tests are used for assessment of the qualitative and quantitative aspects of chemical transport in disturbed and undisturbed soil columns and lysimeters [10, 11, 15]. These tests give information on response of hydrodynamic dispersion (D) to soil physical characteristics, diffusion and ion changes and sorption in soils. For example, asymmetric BTCs obtained from miscible displacement of a nonreactive solute (i.e., chloride) indicate effect of physical nonequilibrium on solute transport. Physical nonequilibrium arises when soil water content, properties of soil texture, structure and pore-size

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distribution exhibit a nonuniformity in transport paths [5, 16]. Due to the weak interaction between soil and nonreactive chemicals such as Cl, Br and NO_3 , physical nonequilibrium is generally the principal source of nonuniformity in the transport of nonreactive chemicals [16, 17].

Interactions between adhesive forces (forces arising from affinity of water molecules to particle surfaces) and cohesive forces (forces arising from affinity between water molecules) results in capillary forces that bind water in pores. Pore-size and water surface tension are two principal factors determining the strength of capillary binding of water in these pores [18]. Changes in surface tension of water may result in altered capillary forces. Therefore, decreased surface tension due to contamination of soil water by surfactants may cause decreased capillary forces in pores. The decreased capillary forces may induce changes in solute transport characteristics. To our knowledge, this notion has not been tested to date. Therefore, this study aimed to evaluate the effect of soil water surface tension on bromide transport in repacked sand columns with different particle-size distribution.

2. Materials and Methods

2.1 Miscible Displacement Tests

MD tests were conducted using disturbed sand columns. Plastic columns (30 cm long and 8.5 cm wide) were packed with sands screened through 2-1, 1-0.5 and 0.5-0.25 mm screens. To avoid preferential flow between column walls and sand material, the column walls were sealed with a silicon insulator. Lower end of the sand columns were supported with a fabric. The MD tests were conducted on four different particle sized sand and four different surface tension adjusted (72.8, 64.0, 53.5 and 42.0 dyne/cm^2) effluents. Each test was replicated four times (total 64 MD tests).

The sand column was gradually saturated with a 0.01 M CaCl_2 solution from the bottom [10]. After saturation, the column was connected to a Mariotte system and the outlet at the bottom was connected to

an automatic fraction collector. Steady state water flow was set with tracer solution of 0.01 N CaCl_2 under zero column water potential. After steady state flow was established, approximately three pore volumes of surface tension adjusted tracer solution of 0.05 M KBr was applied to displace CaCl_2 and then three pore volumes of 0.01 N CaCl_2 was applied to displace the KBr solution from the column [8]. The effluent was collected with the fraction collector and analyzed for bromide with a bromide specific electrode. Following the miscible displacement tests, the sand column was removed and placed in an oven with a constant temperature of 105 °C to determine its bulk density. Relative concentrations (C/C_0) of Br were calculated by dividing the concentration of Br in collected effluent by the concentration of the Br in stock solution. Dimensionless pore volumes were plotted against dimensionless concentrations of Br measured in the collected effluent to obtain a BTC for the corresponding MD test.

The surface tensions of effluent used in the MD tests were decreased with TIMSENTM. First, we conducted four replicated MD tests with original solution of 0.05 M KBr (surface tension unchanged solution) on each of columns repacked with 2-1, 1-0.5 and 0.5-0.25 mm sand sizes (16 MD tests). This was our control test. Then we lowered surface tension of KBr solution to 64 dyne/cm^2 and conducted four replicated MD with this solution on columns repacked with the same sand sizes (16 MD tests). We repeated the test with 53.3 dyne/cm^2 (16 MD tests) and 42 dyne/cm^2 (16 MD tests). All 64 MD tests were conducted under zero soil water potential. The BTCs were evaluated by the CDE model. The computer model STANMOD [19] was used to model BTCs. Pore-water velocity v was measured on the columns, coefficient of hydrodynamic dispersion (D) was predicted and dispersivity (λ) was calculated by $\lambda = v/D$.

3. Results and Discussion

Response of pore water velocity (v) and coefficient

of hydrodynamic dispersion (D) to effluent surface tension (σ) was highly inconsistent across sand particle-sizes (d). The v responded to σ similarly at 1.0-2.0, 0.5-1.0 and 0.25-0.5 mm sizes and differently at $d < 0.25$ mm (Table 1). v and D behaved similarly across σ at d of 0.5-0.25 mm and 2-1 mm, while they behaved considerably differently at 1-0.5 mm particle size.

The σ controls water retention in capillaries. Decreased σ is expected to result in a decreased water retention according to capillary rise equation [18]. Interactions between v and d and between D and d across applied σ were highly inconsistent. Variable v behaved similarly at 53.5 dyne/cm² and 42.0 dyne/cm², and completely differently at 73.8 dyne/cm² and 64.0 dyne/cm²; and D responded differently to changed d at 73.8 dyne/cm² from the rest of the applied σ . In addition, both v and D behaved similarly at 53.5 dyne/cm² and 42.0 dyne/cm². This indicated that D was correlated with v more strongly at lower values σ . Coefficient of hydrodynamic dispersion is resulted from molecular diffusion of solutes from a greater concentration region to a lower concentration region and nonuniform flow of water and solutes in the flow paths [10, 16, 17, 19]. The combined effect of

dispersion and diffusion is represented by D :

$$D = D_m + D_o \quad (1)$$

where, D_m is mechanical dispersion coefficient and D_o is the molecular diffusion coefficient in equilibrium CDE model [20]. Thus, molecular diffusion in the bulk solution and tortuosity of the porous medium (ξ) are important determinants of D . Koestel et al. [21] reported a positive correlation between water flux rate (q) and D from large number of studies. In addition, the solute dispersion scales with the first power of velocity of water in capillary tubes [22]. We found no significant relation between v and d , suggesting that changed σ added more complexity to interrelation between D and corresponding v .

In CDE, model local dispersion is a physical mechanism of spreading caused by micro-scale variability in the velocity field [23]. Ratio of D to pore water velocity (dispersivity) is an important quantity that determines whether the transport is convection or hydrodynamic dispersion dominated. In majority of the cases, the transport was convection dominated (Table 1). Response of λ to σ was similar at 63.5 dyne/cm² and 42 dyne/cm², while it was quite dissimilar at 73.8 dyne/cm² and 53 dyne/cm². In general, λ increased against decreased particle-size.

Table 1 Column properties and measured and estimated solute transport variables.

Surface tension (dyne/cm ²)	Sand size (mm)	D (cm ² /day)	v (cm/day)	λ (cm)
72.8	2-1	461.4	606.3	0.76
	1-0.5	203.52	683.1	0.29
	0.5-0.25	131.2	422	0.31
	< 0.025	172.1	174.8	0.98
64	2-1	131.14	303.1	0.43
	1-0.5	283.6	162	1.75
	0.5-0.25	149.84	220.05	0.68
	< 0.025	128.9	150.8	0.85
53.5	2-1	151.6	188.9	0.80
	1-0.5	246.26	257.31	0.95
	0.5-0.25	73.81	71.5	1.03
	< 0.025	56.43	11.74	4.8
42	2-1	57.96	229.7	0.25
	1-0.5	133.65	284.23	0.47
	0.5-0.25	29.5	152.2	0.19
	< 0.025	165.8	363.1	0.45

D : Coefficient of hydrodynamic dispersion; v : pore water velocity; λ : dispersivity.

Koestel et al. [21] reported a larger λ for decreased soil particle-sizes, which is consistent with our results.

Results of many studies have showed consistent relations between particle-size distribution and v and between v and D . As stated above, relationships among d , v and D were highly inconsistent in our study. Differences in pore-geometry caused during packing of the columns would also cause some variations in v and D . However, we attributed the discrepancies between d and v , d and D , v and D to non-uniform effect of changed σ on the solute transport at different pore-size distribution.

4. Conclusions

Pore-size is an important mediator of solute transport in a porous medium. Surfactants can affect the physics of water retention and flow in soil systems, altering contact angle and surface tension. We studied response of solute transport variables in CDE model (v , D and λ) to changed σ across different sand d on repacked sand columns. Response of λ , D and v to decreased σ was highly inconsistent across applied d . The values of λ were mainly negatively correlated with particle-size across the studied σ . Unexpectedly, decreased σ resulted in a reduced water flow and decreased dispersion in majority of cases in all the studied sand sizes. The results indicated that surfactant contaminated effluents may behave differently from uncontaminated effluents in identical porous media.

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