

VISUALIZATION OF COLLOIDAL TRANSPORT IN POROUS MEDIA

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Summary

Hydrophobic and hydrophilic colloid breakthrough experiments were conducted with unaltered hydrophilic and weakly water repellent sand. While the concentration of colloids in the outflow water was measured, pore-scale observations of colloid distribution were also made. These experiments reveal the relative importance of the various sorption mechanisms of colloids in porous media. Sorption at the air-water interface except near the solid interface, did not appear to affect the retention of colloids. The findings form an essential link between Darcy scale colloid transport and pore-scale retention.

Introduction

Transport and retention of colloids in the subsurface environment has received considerable attention in recent years (Wan and Tokunaga, 1997). In addition to conventional straining and physical-chemical adsorption (McDowell-Boyer et al., 1986), colloid retention in unsaturated porous media has been attributed to attachment at the air-water (AW) interface. Employing etched glass micro models in pore-scale visualization studies, Wan and Wilson (1994) demonstrated the potential for irreversible sorption of colloids onto stationary AW interface. Subsequent studies in the unsaturated zone have also linked reduced colloid concentrations in the column drainage water to sorption at the AW interface (Schafer et al., 1998; Jewett et al., 1999; Jin et al., 2000). However, these conclusions were based on Wan and Wilson's earlier observations with glass micro models, and none of these studies have visually confirmed evidence of colloids sorption on the AW interface. In this presentation, we describe a pore-scale visualization technique that can be used with real sands to observe the distribution of colloids. We will use this technique to compare colloid transport and retention in two types of sands with literature results obtained with micro models.

Materials and Methods

The experimental setup included an infiltration chamber, light source, electro-optical equipment (lens, camera and computer system) and imaging software (Fig. 1). The electro-optical equipment included a Zoom 6000 II lens assembly with 1X adapter (D.O. Industries, Inc.) and color charged-coupled device camera (Cohu, Inc.). An IBM-compatible computer, monitor, frame grabber card (Scion Corp.) and Scion Image software were used for image processing and display. Maximum image resolution for the complete system was 212,000 square pixels per 1 mm². In addition to capturing still digital images with Scion Image, a videocassette recorder and monitor were used to gather continuous real-time images for subsequent review and analysis. Several sets of experiments were performed with this visualization system. The viewing area was illuminated using a variable intensity, 150-W tungsten-halogen lamp with fiber optics cable (D.O. Industries, Inc.).

Twelve colloid breakthrough experiments were completed (six with unaltered hydrophilic sand and six with water-repellent sand), producing six sets of replicate experiments with hydrophilic colloids, hydrophobic colloids and no colloids. Non-fluorescent, blue-dyed polystyrene latex microspheres (Magsphere, Inc.) comparable in size to *Cryptosporidium parvum* oocysts (mean diameters of 4.8 and 5.2 μ m) were used in the experiments. The surfaces of the colloids were either negatively charged (4.8 μ m carboxylated) or uncharged (5.2 μ m underivatized) latex with hydrophilic and hydrophobic surface characteristics, respectively. Hydrophilic sand consisted of translucent quartz sand (Unimin Corp.), with grain diameters equivalent to 0.85 - 1.70 mm and was washed and rinsed 10 times in distilled water to remove loose surface impurities. Weakly water repellent sand with a negative matric entry value was made with the recipe of Bauters et al,

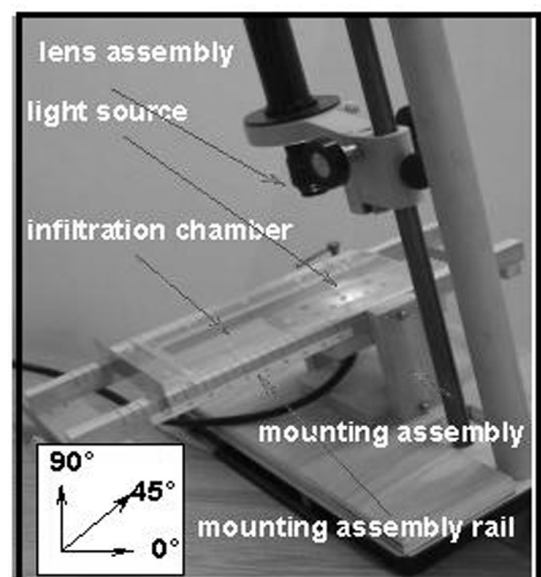


Fig 1: Principal components of the experimental setup. Not shown are the CCD camera and the computer system.

(1998) and consisted of a mixture of 0.4% extremely water repellent grains with hydrophilic sand for the remainder.

The infiltration chamber was constructed from 0.5 cm thick, clear acrylic sheets. Interior dimensions of the chamber were 26.0 cm high, 4.8 cm wide and 0.5 cm deep. The front plate interfered with the image analysis and was mounted with bolts and wing nuts for disassembly after the sand was added. The infiltration chamber was supported on a mounting assembly at 45° incline from horizontal and perpendicular to the focus of the camera. Forty-five degree inclination was chosen to maximize gravitational effects while preventing erosion of the packed-sand layers during infiltration and drainage. The viewing area was adjusted across the camera by sliding the chamber along rails on the mounting assembly. After the chamber was filled, one pore volume (PV, ~ 26 ml) of distilled, deionized (2D) water (0.1 mM CaCl₂ and pH 5.6) was delivered through the sampling port at an inlet flow rate of 2 ml/min. With the sand completely wetted, the chamber was placed on an inclined mounting assembly and left to drain undisturbed for 30 min.

A suspension of either the hydrophilic or hydrophobic microspheres at a concentration of $\sim 3 \times 10^5$ particles/ml (in a solution of 0.1 mM CaCl₂ and pH 5.6) was applied as a point source on the top layer of sand using a peristaltic pump. One PV of colloidal suspension was delivered at a flow rate of 2 ml/min. Two PV water of the same ionic strength and pH immediately followed the colloidal suspension at the same application rate. Effluent from the sampling port was collected every minute during the 3 PV injection sequence. The samples were analyzed by measuring absorbance at 380 nm using a spectrophotometer (Bausch and Lomb, Inc.). No correction for background levels were required because absorbance in effluent samples from the control experiments was negligible.

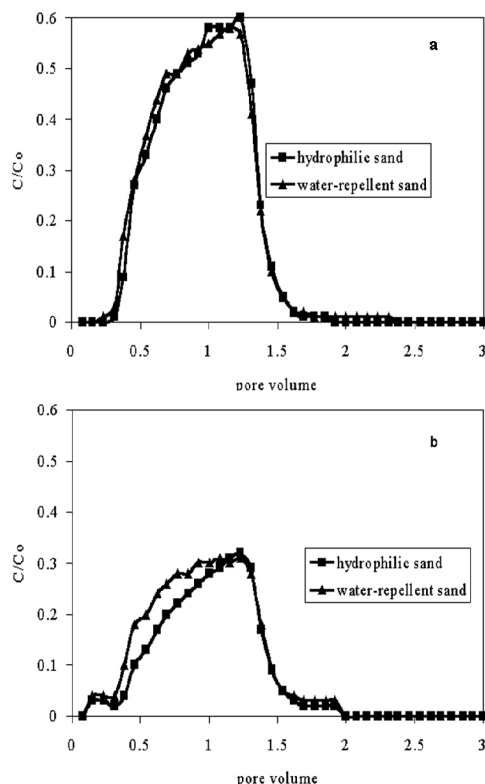


Figure 3: Colloid breakthrough in hydrophilic (solid squares) and hydrophobic sand (solid triangles) for a: hydrophilic colloids; b: hydrophobic colloids.

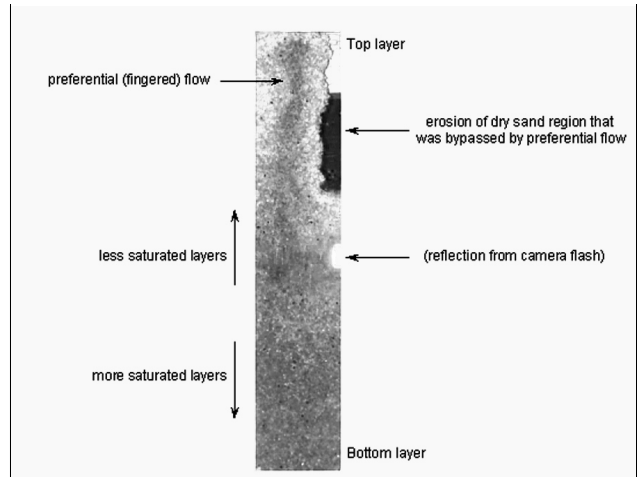


Figure 2: An image of the chamber with hydrophilic sand after application of hydrophobic colloids and water, showing the distribution of the colloids (darker shade) within the preferential (fingere) flow path.

Results and Discussion

Moisture contents were determined after 30 min of drainage and ranged from 0 at the top layer to $0.37 \text{ cm}^3 \text{ cm}^{-3}$ at the lowest depth directly after the infiltration period. Three zones can be delineated: 0 to $\sim 0.08 \text{ cm}^3 \text{ cm}^{-3}$ for the 0 - 14 cm depth, ~ 0.08 to $\sim 0.29 \text{ cm}^3 \text{ cm}^{-3}$ for the 14 - 19 cm depth and ~ 0.29 to $0.37 \text{ cm}^3 \text{ cm}^{-3}$ for the 19 - 25 cm depth. Standard deviations in moisture contents were highest in the intermediate and lower zones. Although the infiltration pattern was different for the two sands, the type of colloid did not affect the infiltration pattern. Infiltration in the unaltered hydrophilic sand produced one fingere flow path for colloid and water movement, measuring ~ 2 cm width in the upper packed-sand layers and increasing to the width of the chamber at 11 - 13 cm depth (Fig. 2). Infiltration experiments with the weakly water repellent sand was different from hydrophilic sand with the water and colloids distributed through the width of the chamber within 2 - 4 cm from the point of application. The colloid breakthrough curves were significantly different for the hydrophilic and hydrophobic colloids but surprisingly the type of sand did not affect it (Fig. 3). The latter indicated that the effective pore volume for leaching was approximately equal for the two sands. Breakthrough of hydrophilic colloids was first detected at 0.3 PV (Fig. 3a) and effluent concentrations increased steadily to a peak value at 1.2 PV. Colloid concentrations declined rapidly from 1.2 to 1.5 PV, coinciding with the step change in the input of the colloid-free solution. Deposited colloids were almost all retained in the sand during the flush of the

colloid-free solution as indicated by the minimal tailing in the breakthrough curve (BTC) from 1.5 to 1.9 PV and undetectable levels of colloids thereafter. The percent of hydrophilic colloid mass recovered in the effluent was 50% for the replicate columns. In contrast to the hydrophilic colloids, the BTC for the hydrophobic colloids rose more slowly and tapered off to a plateau at effluent concentrations considerably lower than those observed for the hydrophilic colloids (Fig. 3b). Hydrophobic colloids appeared in the effluent at 0.2 PV, gradually increasing to a peak concentration at 1.2 PV. This breakthrough was slightly earlier in comparison to hydrophilic colloids. Following application of colloid free solution, hydrophobic colloids concentrations decayed sharply but showed significant tailing indicating the release of attached colloids from 1.5 to 1.9 PV. No mobile or re-mobilized colloids were detected in the effluent samples after 2 PV. Only 25% of the total mass of hydrophobic colloids was recovered in drainage water with water-repellent sand. The breakthrough curves for replicate experiments were in excellent agreement with the colloid breakthrough studies of Wan et al. (1994) and the modeling results of Corapcioglu and Choi (1996). In the next section we will compare how the

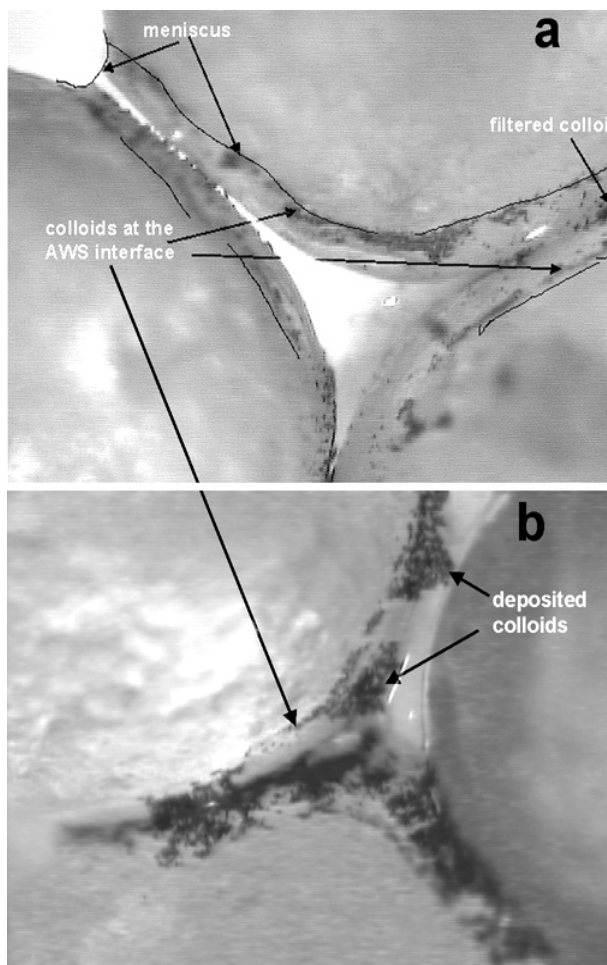


Figure 4: Visualization of colloid distribution in pore space. a: Hydrophilic colloids are deposited mainly at the air-water-solid interface where the meniscus is attached to the sand grain. b: Hydrophobic colloids are mainly deposited within the pendular ring at the water-solid interface with a few at the air-solid water interface

visualizations of Wan and Wilson's micro model compare with our visualizations with sand. This comparison is valid since the same type of breakthrough curves was obtained.

Visualization with the color charged-coupled device camera during colloid addition showed that the hydrophilic colloids were mainly retained near the fringes of the menisci, associated with the air-water-solid (AWS) interface (Fig. 4a). Although the details of the menisci are lost in black and white photographs, it was clear from direct observations that the dark band of colloids was located on the grain surfaces in the pendular ring near the water surface and where the thickness of the water film is the smallest. Although this type of colloid retention could be called "film straining", it is not what is typically thought of in the literature (Wan and Tokunaga, 1997). In addition some of the colloids deposited through gravitational settling and filtration in narrow pore spaces where grain-to-grain contact are present (Fig. 4a, the dark band of colloids where the grains come together). For the hydrophobic colloids (Fig. 4 b), the sedimentation to the grain surface and filtration between grains within the pendular rings was much greater than for the hydrophilic colloids. A small number of the hydrophobic colloids also attached to the AWS interface. The apparently greater retention of the hydrophobic colloids is in agreement with the breakthrough results in Fig. 3. For neither the hydrophilic or hydrophobic colloids, did we find evidence of retention of any colloids at the AW interface (Fig. 4) except near the solid interface where the water depth was smallest (as discussed above) and as "bridges" of coagulated colloids (Fig. 5). These colloid bridges were present in regions where the moisture content was below $0.08 \text{ cm}^3 \text{ cm}^{-3}$ for depths less than $\sim 11 \text{ cm}$, and were less numerous with the hydrophobic than the hydrophilic colloids. To a lesser extent than found with unaltered sand, coagulated colloids or "bridges" were also seen in water repellent sand.

The hydrophobic colloids were re-mobilized after the colloid suspension was switched to colloid-free water, resulting in intermittent release of colloids and coagulated "clusters" of colloids in the pore spaces even after 2.5 PV's. This

re-mobilization process was more apparent with colloids having hydrophobic versus hydrophilic surface properties. The longer descending tails in the BTCs for the hydrophobic colloids (Fig. 3) is consistent with these observations. Especially the colloids attached at the AW interface were resistant to moving under steady state water flow conditions. Despite this, the colloids near the solid water interface were not strongly attached. In a separate experiment with the same visualization equipment we observed colloid concentration near an AW interface similar to Fig. 5. Upon decreasing the flow the meniscus retreated but the colloids remained in place on the grain surface. After increasing the flow rate to the same rate,

the menisci did not come back to the original position and the colloids remained in place. Only after increasing the flow rate several times the meniscus snapped back via a Haynes jump to the original position and swept the colloids away almost instantly. In this case the colloids changed the pore geometry sufficiently so that the water followed a different path with the same flow rate. Breakthrough of hydrophilic colloid and mass recoveries were almost identical for experiments with hydrophilic and water repellent sand. Despite this, there was, on a pore-scale, a difference between the interaction of colloid and the water repellent grains: Colloids seemed to "resist" sedimentation on water repellent sand grains and, in contrast to still and videotape images from unaltered hydrophilic sand grains, showed limited attachment at the AWS interfaces on non-wetting sand grain surfaces. Hydrophilic colloids tended to deposit more readily onto these water repellent grain surfaces than hydrophobic colloids. However there was little effect on the overall breakthrough because only 4 in 1000 grains were water repellent. As water movement is affected by a pressure gradient, a small number of water repellent grains along the flow path will affect the flow pattern as is shown in these experiments (Bauters et al., 2000).

Since visual confirmation was not able to confirm the attachment of colloids at the AW interface, it is of interest to re-examine the Wan and Wilson's two-dimensional, glass micro model images that were the basis for their conclusion. In their paper, the critical region for attachment at the AW interface is centered about the darkened ring on the stationary air bubble (Wan and Wilson, 1994). For a trapped air bubble between narrowly separated, hydrophilic glass plates the distinction between the AW interface and AWS interface is difficult to determine. In other words it cannot be excluded that Wan and Wilson could have interpreted the colloids at the AWS interface as at the AW interface. For Wan and Wilson the distinction between AWS- and AW interface was likely not important: after all the AWS interface is part of the AW interface. Moreover, for static experiments the consequences of assuming that the colloids are either at the AWS or AW interface are inconsequential. However, for colloid breakthrough experiments the assumption is likely consequential considering the following argument. The Reynolds number for water flow in porous media is low enough that the flow is laminar. Under laminar flow theory, the velocity at the solid interface is zero, while it is positive anywhere else including the AW interface away from the solid. Thus, if colloids were retained at the AW interface they would move generally with the water to the outlet. Only colloids on- or near the grain surface are in regions where the water velocity is so slow that the colloids remain near the surface even without firm attachment. This is what we observed.

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Figure 5: Coagulant hydrophilic colloids formed "bridges" between the grains.

