Transport of Barrel and Spherical Shaped Colloids in Unsaturated Porous Media

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Abstract

Model colloids are usually spherical, but natural colloids have irregular geometries. Transport experiments of spherical colloids may not reflect the transport characteristics of natural colloids in porous media. We investigated saturated and unsaturated transport of colloids with spherical and angular shapes under steady-state, flow conditions. A pulse of negatively-charged colloids was introduced into a silica sand column at three different effective water saturations ($S_e = 0.31$, 0.45, and 1.0). Colloids were introduced under high ionic strength of 106 mM to cause attachment to the secondary energy minimum and later released by changing the pore water to low ionic strength. After the experiment, sand was sampled from different depths (0, 4, and 11 cm) for scanning electron microscopy (SEM) analysis and colloid extraction. Water saturation affected colloid transport with more retention under low than under high saturation. Colloids were retained and released from a secondary energy minimum with more angular-shaped colloids being retained and released. Colloids extracted from the sand revealed highest colloid deposition in the top layer and decreasing deposition with depth. Pore straining and grain-grain wedging dominated colloid retention.

Keywords: Colloids, Unsaturated Transport, Colloid Shape, Barrels, Spheres

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1. Introduction

Spherical colloids are often used to study colloid transport in porous media (Bradford et al., 2002; Ma et al., 2011; Knappenberger et al., 2014). While spherical colloids are useful model colloids, natural colloids are seldom spherical but rather have platy, ellipsoidal, and more complex geometries (Kotlyar et al., 1993; Fujita et al., 2003; Mashal et al., 2004; Baltus et al., 2009). Engineered nanoparticles, such as carbon nanotubes, also often have non-spherical shapes (Christian et al., 2008; Tian et al., 2011). The difference in shape affects transport of colloids in porous media because attachment and detachment of colloids to interfaces, both solid-liquid as well as liquid-gas interfaces, depend on the geometry of the interacting interfaces.

Only few studies have been reported where the effect of colloid shape on colloid transport in porous media was investigated explicitly (Weiss et al., 1995; Salerno et al., 2006; Xu et al., 2008; Liu et al., 2010; Seymour et al., 2013), all of which were conducted with saturated porous media. Salerno et al. (2006) compared the transport of spherical (1 μm diameter) and rod-shaped particles (made by stretching the spherical particles) in a medium made of glass beads. As the rod-shaped colloids were made of the same material as the spherical colloids, the surface properties of the two colloid types were the same. More retention of the rod-shaped particles was observed, and the larger the colloids' aspect ratio, the more the colloids were retained. Contrary results were obtained by Liu et al. (2010), who compared transport of spherical and rod-shaped microspheres. Less

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retention of rod-shaped colloids during transport was observed, which was explained by preferential alignment of the rod-shaped colloids along the flow field (Liu et al., 2010). Streamline orientation was also found in saturated and unsaturated transport experiments of single-walled carbon nanotubes (Tian et al., 2011).

Xu et al. (2008) suggested that the larger the aspect ratio of colloids, the more pronounced the alignment of the major axis is with the flow streamlines. The aspect ratio/streamline hypothesis explains, to a certain extent, the difference in the results reported by Salerno et al. (2006) and Liu et al. (2010): the aspect ratio of the rod-shaped colloids was larger (7:1) in the Liu et al. (2010) study compared to the Salerno et al. (2006) study (2:1 and 3:1).

More deposition of spherical colloids compared to rod-shaped colloids under favorable attachment conditions was reported from a quartz microbalance study (Seymour et al., 2013). Less rod-shaped particles were deposited under favorable conditions because greater hydrodynamic forces and torques counterbalance greater attractive forces of rod vs. spherical shaped particles (Seymour et al., 2013). However, less deposition of spherical colloids compared to rod-shaped colloids was found for colloid transport under unfavorable attachment conditions in a porous medium made of glass beads. Under unfavorable attachment conditions an energy barrier is present that prevents colloids from attaching to a primary energy minimum while under favorable attachment conditions such an energy barrier is not present, and colloids can attach to a primary energy minimum. While the literature indicates an effect of particle shape on transport, the reported evidence is inconclusive in regard to the direction of this effect, i.e., whether transport is being enhanced or hindered depending on shape.

Under unsaturated flow, colloid transport is usually impeded by the pres-

ence of the air-water interface (Wan and Tokunaga, 1997; Cherrey et al., 2003; Torkzaban et al., 2008; Mishurov et al., 2008; Mitropoulou et al., 2013; Sang et al., 2013; Knappenberger et al., 2014). Colloid shape is expected to affect colloid transport in unsaturated porous media even more so than under saturated flow conditions, because interactions with the air-water interface are strongly shape-dependent. Capillary forces holding colloids to the air-water interface are greater for non-spherical particles because of larger contact lines forming at non-spherical particles (Chatterjee et al., 2012; Chatterjee and Flury, 2013), and angular shapes cause the air-water interface to get pinned at angular corners of particles, which leads to an increase of capillary forces (Aramrak et al., 2013; Chatterjee and Flury, 2013). Based on this, we expect that angular-shaped colloids will be more retained than spherical colloids during transport in unsaturated porous media.

More complex colloid shapes violate the geometric assumptions in general DLVO calculations of plate-to-plate, plate-to-sphere, or sphere-to-sphere interactions (Elimelech et al., 1995). Non-spherical colloids interacting with a solid surface are relatively challenging to approximate by typical DLVO calculations. To prevent violating these geometric assumptions, non-spherical colloids can be defined as spheres with an effective radius equal to the radius of a surface-area-equal sphere (Salerno et al., 2006). Such an effective radius of a non-spherical particle is larger than that of a spherical particle with the same volume. Bhattacharjee et al. (2000) reported a method to calculate the interaction energies of non-spherical colloids in respect to their orientation to the collector surface. For end-on orientation, the interaction energies between the colloid and the collector decrease, while in side-on orientation the interaction energies increase. Recently, Wu et al. (2013) determined DLVO interactions of carbon nanotubes for arbitrary

tube-plane orientations.

Our objective was to evaluate the effect of colloid shape, specifically angular vs. spherical colloids, on saturated and unsaturated colloid transport in porous media. We hypothesized that the effect of colloid shape is more pronounced under unsaturated than under saturated flow because of enhanced interactions with the air-water interface, and that angular-shaped colloids get pinned at air-water interfaces, thereby getting preferentially retained in the unsaturated porous medium. We carried out colloid transport experiments with spherical and angular-shaped colloids under both saturated and unsaturated flow conditions in a sand medium with effective water saturations S_e of 0.31, 0.45, and 1.0. Spherical and angular-shaped colloids were made of the same material and had the same volume and similar surface properties. Colloid breakthrough curves and colloid depth profiles were measured. Scanning electron microscopy was used to analyze surface coverage of colloids on sand particles.

2. Experimental Methods

2.1. Porous Medium & Column Design

Colloid transport experiments were done with a Plexiglass column with a length of 15 cm and a diameter of 5 cm. The experimental setup was the same as described in Knappenberger et al. (2014). The column was equipped with water content and matric potential sensors at a distance of 4 and 11 cm from the bottom of the column. Time domain reflectometry (TDR) probes were used as water content and tensiometers as matric potential sensors. Silica sand (3382-05, Mallinckrodt Baker, Inc., Phillipsburg, NJ), wet sieved to the fraction between 250 μm and 425 μm and pretreated with 2 M HCl at 90 °C, was used as porous medium. The sand was filled in 1 cm-increments into the column and compacted

by vibration as described by Lewis and Sjoström (2010). The packed medium had a porosity of $\epsilon = 0.35 \text{ cm}^3/\text{cm}^3$ and a bulk density of $\rho_b = 1.72 \text{ g/cm}^3$. The liquids were introduced to the column with a peristaltic pump (IPC 4, Ismatec, Glattbrugg-Zürich, Switzerland). The sand was sonicated, washed in DI water, and repacked after every experiment. Steady-state saturated and unsaturated flow were established by using a porous stone at the top and a constant tension applied through a membrane ($25 \mu\text{m}$ pore size) at the bottom. The tension at the bottom of the column is necessary to maintain a uniform soil water content profile over the whole length of the column.

2.2. Colloid Shapes

We used spherical carboxylate-modified polystyrene colloids with a diameter of $1 \mu\text{m}$ (PC04N/10356, Bangs Laboratories, Inc., Fishers, IN). A batch of the spherical colloids was modified into barrel shape using the protocol described in Champion et al. (2007) and Aramrak et al. (2013). This protocol included several steps of immersion into chemicals and stretching. A batch of spherical colloids was treated in the same manner, but without the stretching step to ensure that all colloids used for the transport experiments underwent the same treatment and had as similar a surface characteristics as possible. Properties of colloids and the sand medium are listed in Table 1, and Scanning Electron Microscopy images are shown in Figure 1 (A,B,C).

2.3. Colloid Transport Experiments

Colloid transport experiments were carried out under steady-state flow at three different water saturations $S_e = 0.31, 0.45$, and 1.0 (Table 2). Each experiment was repeated once. Flow rates and bottom tensions were adjusted in

such a manner that the two TDR sensors and tensiometers read the same values, indicating uniform flow conditions. More details on experimental controls of flow rates as well as TDR and tensiometer readings are given in Knappenberger et al. (2014). A 1 mM NaNO_3 solution was used as a tracer prior to the colloid experiments to check for non-equilibrium conditions and immobile water fractions. We analyzed the nitrate breakthrough curves with CXTFIT (Toride et al., 1999). Experimentally measured and fitted model parameters are listed in Table 2.

Colloids (either spheres or barrels) were suspended in a pH 10 buffered solution (1.67 mM NaHCO_3 , 1.67 mM Na_2CO_3 , and 100 mM NaCl , making the overall ionic strength 106 mM) and introduced as a four pore volume pulse into the column. This high ionic strength was selected to provide conditions of colloid attachment in a secondary energy minimum (see DLVO calculations below). After colloids were eluted with five pore volumes of colloid-free solution, we decreased the ionic strength of the inflow solution to release colloids attached in the secondary energy minimum. The detailed sequence of liquids and pore volume durations is shown in Table 3. This sequence was repeated once for each colloid shape and water saturation.

We measured the colloid concentrations inline with UV-Vis spectrophotometry (CVF-Q-10 flow cell, CUV-UV cuvette holder, QP400-2-SR fiber optics, 200-2000 nm, USB-DT light source, USB-4000 spectrometer, Ocean Optics, Dunedin, FL). We determined calibration curves for nitrate and colloids in all different liquids used. Colloids were quantified at 480 nm wavelength, nitrate at 220 nm wavelength.

In addition to colloid breakthrough curves, we excavated the sand at the end of the experiments at depths of 0, 4, and 11 cm to determine colloid depth

profiles. About 17 g of sand was extracted for attached colloids as described by Bradford et al. (2002). The sand was placed in 50 mL polypropylene centrifuge tubes, 20 mL nano pure water was added, and the tubes were shaken for 10 minutes. The supernatant was then measured for colloids by UV-Vis spectrophotometry. The UV-Vis measurement was corrected for background noise caused by the silica sand itself. This background signal was determined by extracting a colloid-free sand sample.

2.4. Scanning Electron Microscopy

A small fraction of the excavated sand samples was used for scanning electron microscopy (SEM) to visualize and count deposited colloids. These sand samples were air-dried and then coated with platinum and examined by SEM (FEI Quanta 200F, FEI Co., Hillsboro, OR). For quantification of colloids, we choose five sand grains randomly from an image of 2.5 mm by 2.5 mm (Figure 1C). On each grain, we then randomly chose three areas for more detailed investigation (Figure 1D). The random locations were determined by applying a 400 μm by 400 μm lattice to the grain image and choosing random squares within the lattice. The three locations on the sand grains were then magnified so that colloids were clearly visible and an area of 45 μm by 45 μm was selected for further investigation (Figure 1E,F).

On these selected areas (Figure 1E,F), we counted the number of colloids and categorized whether the colloids were deposited as single particles or in clusters of multiple colloids (Figure 1E,F). We further categorized the surface roughness and the topography of the sand surface at the point of attachment as smooth/rough and flat/convex/concave (see Figure 1G,H). Colloids deposition sites were judged by eye as smooth or rough surface (e.g., Figure 1G) and the

topography of the overall region of the deposition site was judged by eye as flat/convex/concave (e.g., Figure 1H). Every deposited colloid was thus given attributes of clustering (yes/no), surface roughness (smooth/rough), and deposition topography (flat/convex/concave). All visual judgement was performed by the same person to assure consistency.

2.5. Statistical Analysis of SEM Data

We used two statistical approaches to process the data that we acquired through scanning electron microscopy: First, we quantified the number of deposited particles as a function of water content and depth. Second, we analyzed whether colloid shape, water content, or depth affected the number of colloids deposited in clusters, on rough surfaces, or on different topographies. The former analysis was performed with a zero-inflated negative binomial model (ZINB) and the latter with logistic models.

Count data contain only non-negative integer values and are therefore often analyzed assuming poisson or negative binomial distribution (Yau et al., 2003). Many of our SEM pictures did not show any colloids which resulted in zero count data. Consequently, our data set contained more zeros than would be expected from a poisson or negative binomial distribution. Therefore we assessed our data with a zero-inflated negative binomial (ZINB) model to account for extra zeros in our data (Zuur et al., 2009; Hilbe, 2014). The ZINB consists of two parts: a logistic part that models whether colloid deposition occurs at all, and a negative binomial part, that models the number of deposited colloids as a function of colloid shape, water content, and depth. Data analysis was performed in R (R Development Core Team, 2013) with the count data regression model `zeroinfl` (Zeileis et al., 2008) from the `pscl` package (Jackman, 2014).

The deposition attributes of our colloids, clustering, surface roughness, and topography were analyzed with separate logistic models. The dependent variables were colloid shape, water content, and depth as well as their interactions. Non-significant factors were removed from the model until only significant factors remained.

2.6. DLVO Calculations

We computed the interaction energy between colloids and the sand particles based on DLVO theory. For the spherical particles we computed sphere-plate interactions as (Gregory, 1975):

$$\Delta G_{\text{el}} = 64\pi r \epsilon \left(\frac{kT}{ez} \right)^2 \gamma_1 \gamma_2 \exp(-\kappa h) \quad (1)$$

and (Gregory, 1981):

$$\Delta G_{\text{vdW}} = \frac{Ar}{6h} \left[1 - \left(\frac{5.32h}{\lambda} \right) \ln \left(1 + \frac{\lambda}{5.32h} \right) \right] \quad (2)$$

where ΔG_{el} is the double layer interaction energy, ΔG_{vdW} is the van der Waals interaction energy, r is the colloid radius, ϵ is the electromagnetic permittivity of the medium, k is the Boltzmann constant, T is the absolute temperature, e is the electron charge, z is the ion valence, γ_1 and γ_2 are the surface potentials, κ is the inverse Debye-Hueckel length, h is the separation distance, A is the Hamaker constant, and λ is the length of interaction. The Hamaker constant between polystyrene and silica sand was taken as $A_{132} = 4.04 \times 10^{-21}$ J (Bradford and Torkzaban, 2008). The ζ -potentials needed for these calculations are listed in Table 1. At the lower ionic strength (nano pure water) the total interaction energy $\Delta G_{\text{TOT}} = \Delta G_{\text{el}} + \Delta G_{\text{vdW}}$ for the spherical polystyrene colloid-silica sand

interaction shows a repulsive energy barrier (Figure S2, supporting information). At the higher ionic strength of $IS = 106 \text{ mM}$, there was a secondary energy minimum present (Figure 2).

We used two approaches to calculate the interaction energy of the barrel-shaped colloids (Bhattacharjee et al., 2000): In the first approach, we calculated an effective radius based on a sphere having the same surface area as the barrels (see Table 1) and then used equations 1 and 2. In the second approach, we determined the orientation-dependent interaction energy as described by Bhattacharjee et al. (2000) and Liu et al. (2010). The orientation-dependent interaction energy is computed for the extreme cases of the barrel shaped particle being oriented with its end towards a plate (end-on), and with its side (side-on) towards the plate. Side-on and end-on orientations are considered to mark the extremes, and therefore, any other orientation will result in interaction energies in between these two extremes. There was a pronounced energy barrier and a secondary energy minimum at high ionic strength for both orientations (Figure 2).

3. Results and Discussion

3.1. Nitrate Breakthrough Curves

The flow in our experiments occurred under equilibrium conditions without flow stagnation zones according to the analysis of the nitrate breakthrough curves (Figure S1, supporting information) with CXTFIT. The modeled pore water velocity v matched well with the measured data (Table 2).

3.2. Colloid Transport

Figure 3 shows the colloid breakthrough curves for the different water contents. Under high ionic strength conditions, more spherical colloids were trans-

ported under saturated than under unsaturated flow conditions. No colloid transport occurred at a low effective saturation of $S_e = 0.31$. Spheres showed more pronounced transport than the barrels, indicating that barrels were more effectively retained in the porous medium.

After the inflow was changed to low ionic strength, colloids were released, with the most distinct release observed for the barrels (Figure 3). The interaction energy profiles from DLVO calculations revealed a primary energy barrier and a secondary energy minimum for both colloid shapes under high ionic strength (Figure 2). No secondary energy minimum was present under low ionic strength (Figure S2, supporting information). The presence of a secondary energy minimum explains the retention of colloids and the subsequent release of colloids after the ionic strength was reduced. A larger amount of barrels was released because more barrels were initially immobilized in comparison to the spheres.

The calculated DLVO profiles differ depending on the calculation method (Figure 2). The curves computed from an effective radius are similar to the curves for the spheres (because the radii did not differ much, see Table 1), but the orientation-dependent interaction energies differed substantially between end-on and side-on orientation. The energy barrier and the secondary energy minimum are smaller in magnitude for end-on orientation in comparison to spherical particles. In this orientation, less particles would be retained in a secondary energy minimum in comparison to spherical particles. But the magnitude of energy barrier and secondary energy minimum are larger if the barrels are oriented side-on. The side-on orientation would therefore lead to more colloid retention in the secondary minimum, which is consistent with the results of the column experiments where a larger amount of barrels vs. spheres was released due to the change of ionic strength.

Mass balance calculations from the colloid breakthrough and release curves revealed that even under saturated conditions only a fraction of the colloids were recovered from the column (Table 2) and more than 75% remain retained even after the decrease of the ionic strength. Experiments conducted with the same medium but with smaller colloids (220 nm diameter) resulted in recovery of 100% of the colloids under saturated conditions (Knappenberger et al., 2014). Pore straining (Bradford et al., 2002, 2004) and grain-grain wedging (Johnson et al., 2007) are considered to occur if the colloid-to-grain ratio exceeds a threshold of 0.0017 to 0.005 under saturated conditions. In our experiments, the colloid-to-grain ratio was 0.0018 to 0.0054 which makes straining and wedging likely mechanisms for colloid retention under saturated flow. Under unsaturated flow conditions, colloids are likely also strained and wedged between solid-water and air-water interfaces.

3.3. Colloid Depth Profiles

Figure 4 shows the depth profiles of colloids in the sand columns. The data represent results from the SEM particle count and concentration measurements from extracted sand samples. The SEM count data are shown as box plots for the corresponding depths. The count data were normalized by dividing by the effective saturation to account for the different amounts of colloids introduced by the four pore volume pulse. Overall 270 SEM images were processed of which 92 images contained no colloids. The largest number of colloids in one image was 319. The numbers of colloids measured by batch extraction, N_c , were also normalized by the amount of introduced colloids, N_{tc} , and the mass of the dry sand of the measured batch resulting in a relative amount of colloids per mass of sand. Deposition generally decreased with increasing depth, except for the

saturated conditions where deposition was more uniform with depth. More particles were found under dryer conditions indicating that lower water saturation increased colloid deposition.

More colloids were retained under unsaturated conditions with significant more deposition in the top layer ($z = 0$) and decreasing colloid concentration for the layers $z = -4$ and $z = -11$ cm (Figure 4B, 4C, 4E, 4F). Similar depth profiles were reported by other authors (Bradford et al., 2006; Torkzaban et al., 2008). Bradford et al. (2006) conducted experiments under different flow rates and ionic strengths and found that exponential depth profiles only occurred under high ionic strength of 56 mM as opposed to low ionic strength of 6 mM. Torkzaban et al. (2008) conducted experiments under saturated and unsaturated conditions and the deposition of colloids on the top layer increased with decreasing water content. Bradford et al. (2006) and Torkzaban et al. (2008) attributed these effects to pore straining, while Wan and Tokunaga (1997) attributed these effects to film straining. Film straining is only relevant if pendular rings are disconnected or films are thinner than the colloid radii. For the same porous medium as used here, we have previously calculated conditions where pendular rings become disconnected, depending on the contact angle of the pore water and the porous medium (Knappenberger et al., 2014). According to these previous results, film straining is not a relevant mechanism at any of the water contents used in our current study. Pore straining and wedging between solid-water and air-water interfaces are therefore likely more dominant deposition mechanisms. Pore straining is indeed possible given our particle-to-grain ratio, as mentioned above.

The differences in the depth profiles between barrels and spheres are small, and we thus conclude that the colloid shape had no effect on deposition caused

by straining or wedging. The only difference observed in the transport of the two colloid shapes was in the attachment in the secondary energy minimum as discussed above.

The logistic part of the zero-inflated negative binomial model describes whether colloid deposition occurs at all. Colloid shape and sampling depth were significant for the logistic part of the model (Table 4). A negative estimate value of -1.55 for the factor “shape” indicates that it is more likely to have zero particle counts in the SEM image for barrels than for spheres. An estimate value of 0.17 for “depth” indicates that the likelihood of zero particle observation increases with sampling depth.

The negative binomial part of the model describes the amount of deposited particles in the SEM images. A positive value of the dispersion parameter θ (Table 4) indicates that the model has adjusted for overdispersion of the data (Hilbe, 2014) which occurs when the variance of a data set is larger than anticipated by the model distribution. Colloid shape, water content, and sampling depth, as well as the interactions “shape:depth” and “watercontent:depth” were significant (Table 4). The data indicate that more spheres were deposited compared to barrels, and that colloid deposition decreased with increasing water content and increasing depth. This means that colloid deposition was highest for spheres at a depth of $z = 0$ and an effective saturation of $S_e = 0.31$.

3.4. Colloid Deposition Attributes

The colloid deposition sites were categorized in clustering, surface roughness, and topography. Similar amounts of colloids for both shapes were clustered ($71 \pm 31\%$ for barrels and $67 \pm 32\%$ for spheres; errors are standard deviations). Clustering, for both colloid shapes, increased with increasing water con-

tent ($63 \pm 28\%$, $70 \pm 38\%$, and $78 \pm 29\%$ for barrels, and $52 \pm 31\%$, $64 \pm 33\%$, and $81 \pm 26\%$ for spheres, for water saturations of 0.31, 0.45, and 1.0, respectively). Deposition on rough surfaces varied with water content ($53 \pm 41\%$, $58 \pm 36\%$, and $46 \pm 43\%$ of barrels, $20 \pm 22\%$, $53 \pm 39\%$, and $41 \pm 39\%$ for spheres, for water saturations of 0.31, 0.45, and 1.0, respectively), but there was no distinct trend.

Most of the colloids were deposited on a concave topography ($49 \pm 36\%$ for barrels, and $61 \pm 27\%$ for spheres), followed by flat ($22 \pm 35\%$ for barrels and $26 \pm 29\%$ for spheres), and convex ($29 \pm 32\%$ for barrels and $12 \pm 14\%$ for spheres) topography. The change of water content did not affect the amount of colloids deposited on concave topographies. However, with increase of water content, deposition increased on convex and decreased on flat topography. This effect was more distinct for barrels than for spheres. Although we can delineate some trends as discussed above, the attribute data have large standard deviations, so that differences were statistically not significant.

The deposition attributes surface roughness, clustering, and topography were proportional data for every SEM image, and we therefore used logistic modeling (Crawley, 2012) to analyze the effects of colloid shape, water content, and depth on these deposition attributes. No significant factors were found for surface roughness which means that we cannot correlate deposition to surface roughness from our experimental data. We assessed surface roughness only qualitatively, but other authors also used quantitative approaches, e.g. vertical scanning interferometry (Darbha et al., 2010, 2012) to determine the surface roughness. However, we do not believe that a quantitative approach necessarily would have lead to better correlations of deposition and surface roughness. With our approach we may have not been able to detect colloids at the site where they were

deposited initially (see discussion of limitations below).

Colloid count, water content, and depth were significant factors in the clustering model (Table 5). But colloid count depends on the deposition depth, with more deposited colloids in shallow depths. The statistical model allows us to keep the colloid count data at a constant value and assess the effects of water content and depth. We predicted the likelihood for clustering for a depth-constant colloid count of 77 particles, which is the mean colloid count over all depths, water contents, and shapes. For saturated conditions the likelihood for colloid clustering was fairly constant (0.89, 0.89, and 0.90 for depths 0, -4, and -11 cm, respectively). Under unsaturated conditions, the likelihood for colloid clustering decreased for increasing depths (0.80, 0.62, and 0.25 for depths 0, -4, and -11 cm, and $S_e = 0.31$, respectively). This phenomenon could be a form of filter ripening effect as described by Yao et al. (1971) and Tien and Payatakes (1979). There was no significant difference in the clustering of barrels and spheres, so colloid shape did not appear to affect whether deposited colloids formed clusters.

The topography of the colloid deposition sites was categorized as convex, concave, or flat. Any of these three categories was assessed in a separate logistic model. The logistic model for flat topography assessed the fraction of flat topography in the overall amount of deposited colloids. Corresponding logistic models were created for convex and concave deposition sites.

None of the factors were significant for the flat topography model, so no model data can be reported. However, for the convex and concave topography models, the factors shape and water content were significant (Table 5). More barrels were deposited on convex topography while more spherical colloids were deposited on concave topography. We assume that the pore water velocity is

higher on a convex than on a concave surface. If barrels reside side-on on the collector surface they may expose a smaller cross-sectional area as a spherical colloid. Consequently, a spherical colloid may be dragged further on a convex surface than a barrel-shaped colloid, and therefore deposition of barrels is more likely on convex surfaces while spheres are dragged into concave areas where they experience more flow stagnation zones.

The analysis of the SEM images has several limitations: First, the deposition attributes were acquired qualitatively by visual judgement of SEM images. This approach is somewhat subjective. We tried to minimize errors associated with subjective attribute assignments by having all images analyzed by the same person. Second, preparation of the sand samples for SEM imaging, e.g., excavation of sand grains from column, mounting of grains on SEM stubs, and air-drying, may have disturbed the original configuration of colloids on the sand grains. Therefore, we may not have been able to detect the original deposition sites of the colloids with this approach. Third, we only assessed a small fraction of the overall sand grain surface with the SEM approach. This limitation was overcome to some extent by our randomization approach and the statistical analysis that allowed us to quantify uncertainties.

4. Conclusions

Colloid transport was affected by saturation and more colloids were retained in the column under low saturation conditions. The shape of the colloids (barrels vs spheres) had only little effect on the number of retained colloids and pore straining and wedging affected colloid retention to a larger extent. However, significantly more angular-shaped colloids were retained in a secondary energy minimum at high ionic strength conditions and were released when pore water

chemistry was changed to low ionic strength. This is consistent with DLVO calculations of non-spherical colloids with side-on orientation being exposed to a larger secondary energy minimum in comparison to spherical colloids.

Statistical analysis of the amount of deposited colloids with a zero-inflated negative binomial model revealed that deposition of spherical colloids was more likely and that deposition decreased with increase of column depth. The colloid deposition attributes clustering, surface roughness, and topography differed in their impact on colloid deposition. Clustering was affected by water content and sampling depth, but the shape of the colloids had no significant effect. The topography categorized as convex, concave, and flat surfaces affected colloid deposition with more angular-shaped colloids deposited on convex and more spherical colloids deposited on concave topography. We attribute these effects to different pore water velocities of convex and concave topographies and different cross-sectional areas of angular-shaped and spherical shaped particles that is exposed to pore water flow. Overall, pore straining and grain-grain wedging were dominating the retention of colloids in our experiments.

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- Aramrak, S., Flury, M., Harsh, J. B., Zollars, R. L., Davis, H. P., 2013. Does colloid shape affect detachment of colloids by a moving air-water interface? *Langmuir* 29 (19), 5770–5780.
- Baltus, R. E., Badireddy, A. R., Xu, W., Chellam, S., 2009. Analysis of configurational effects on hindered convection of nonspherical bacteria and viruses across microfiltration membranes. *Ind. Eng. Chem.* 48 (5), 2404–2413.
- Bhattacharjee, S., Chen, J. Y., Elimelech, M., 2000. DLVO interaction energy between spheroidal particles and a flat surface. *Colloids Surf. Physicochem. Eng. Aspects* 165 (1-3), 143–156.
- Bradford, S. A., Bettahar, M., Simunek, J., van Genuchten, M. T., 2004. Straining and attachment of colloids in physically heterogeneous porous media. *Vadose Zone J.* 3 (2), 384–394.
- Bradford, S. A., Simunek, J., Bettahar, M., van Genuchten, M. T., Yates, S. R., 2006. Significance of straining in colloid deposition: Evidence and implications. *Water Resour. Res.* 42 (12).
- Bradford, S. A., Torkzaban, S., 2008. Colloid transport and retention in unsaturated porous media: A review of interface-, collector-, and pore-scale processes and models. *Vadose Zone J.* 7 (2), 667–681.
- Bradford, S. A., Yates, S. R., Bettahar, M., Simunek, J., 2002. Physical factors affecting the transport and fate of colloids in saturated porous media. *Water Resour. Res.* 38 (12).
- Champion, J. A., Katare, Y. K., Mitragotri, S., 2007. Making polymeric micro- and nanoparticles of complex shapes. *Proc. Natl. Acad. Sci. USA* 104 (29), 11901–11904.
- Chatterjee, N., Flury, M., 2013. Effect of particle shape on capillary forces acting on particles at the air-water interface. *Langmuir* 29 (25), 7903–7911.
- Chatterjee, N., Lapin, S., Flury, M., 2012. Capillary forces between sediment particles and an air-water interface. *Environ. Sci. Technol.* 46 (8), 4411–4418.
- Cherrey, K. D., Flury, M., Harsh, J. B., 2003. Nitrate and colloid transport through coarse Hanford sediments under steady state, variably saturated flow. *Water Resour. Res.* 39.
- Christian, P., Von der Kammer, F., Baalousha, M., Hofmann, T., Jul. 2008. Nanoparticles: structure, properties, preparation and behaviour in environmental media. *Ecotoxicology* 17 (5), 326–343, wOS:000256314700002.
- Crawley, M. J., 2012. *The R Book*, 2nd Edition. Wiley, West Sussex, United Kingdom.
- Darbha, G. K., Fischer, C., Luetzenkirchen, J., Schaefer, T., 2012. Site-specific retention of colloids at rough rock surfaces. *Environ. Sci. Technol.* 46 (17), 9378–9387.
- Darbha, G. K., Schaefer, T., Heberling, F., Luetge, A., Fischer, C., 2010. Retention of latex

- colloids on calcite as a function of surface roughness and topography. *Langmuir* 26 (7), 4743–4752.
- Elimelech, M., Gregory, J., Jia, X., Williams, R. A., 1995. *Particle Deposition and Aggregation*. Butterworth-Heinemann, Waltham, MA.
- Fujita, T., Sugiyama, D., Swanton, S., Myatt, B., 2003. Observation and characterization of colloids derived from leached cement hydrates. *Journal of Contaminant Hydrology* 61 (1–4), 3 – 16, 8th International Conference on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere - Migration 01.
- Gregory, J., 1975. Interaction of unequal double layers at constant charge. *J. Colloid Interface Sci.* 51 (1), 44–51.
- Gregory, J., 1981. Approximate expressions for retarded van der Waals interaction. *J. Colloid Interface Sci.* 83 (1), 138–145.
- Hiemenz, P. C., Rajagopalan, R., 1997. *Principles of Colloid and Surface Chemistry*, 3rd Edition. M. Dekker, New York.
- Hilbe, J. M., 2014. *Modeling Count Data*. Cambridge University Press, New York New York, NY.
- Jackman, S., 2014. *pscl: Classes and Methods for R Developed in the Political Science Computational Laboratory*, Stanford University. Department of Political Science, Stanford University, Stanford, California.
- Johnson, W. P., Li, X., Yal, G., 2007. Colloid retention in porous media: Mechanistic confirmation of wedging and retention in zones of flow stagnation. *Environ. Sci. Technol.* 41 (4), 1279–1287.
- Knappenberger, T., Flury, M., Mattson, E. D., Harsh, J. B., 2014. Does water content or flow rate control colloid transport in unsaturated porous media? *Environ. Sci. Technol.* 48 (7), 3791–3799.
- Kotlyar, L., Deslandes, Y., Sparks, B., Kodama, H., Schutte, R., 1993. Characterization of colloidal solids from Athabasca fine tails. *Clays and Clay Minerals* 41 (3), 341–345.
- Lewis, J., Sjöström, J., 2010. Optimizing the experimental design of soil columns in saturated and unsaturated transport experiments. *J. Contam. Hydrol.* 115 (1–4), 1–13.
- Liu, Q., Lazouskaya, V., He, Q., Jin, Y., 2010. Effect of particle shape on colloid retention and release in saturated porous media. *J. Environ. Qual.* 39 (2), 500–508.

- Ma, H., Pazmino, E., Johnson, W. P., 2011. Surface heterogeneity on hemispheres-in-cell model yields all experimentally-observed non-straining colloid retention mechanisms in porous media in the presence of energy barriers. *Langmuir* 27 (24), 14982–14994.
- Mashal, K., Harsh, J. B., Flury, M., Felmy, A. R., Zhao, H., 2004. Colloid formation in Hanford Sediments reacted with simulated tank waste. *Environ. Sci. Technol.* 38 (21), 5750–5756.
- Mishurov, M., Yakirevich, A., Weisbrod, N., 2008. Colloid transport in a heterogeneous partially saturated sand column. *Environ. Sci. Technol.* 42 (4), 1066–1071.
- Mitropoulou, P. N., Syngouna, V. I., Chrysikopoulos, C. V., 2013. Transport of colloids in unsaturated packed columns: Role of ionic strength and sand grain size. *Chem. Eng. J.* 232, 237–248.
- R Development Core Team, 2013. *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria.
- Salerno, M. B., Flamm, M., Logan, B. E., Velegol, D., 2006. Transport of rodlike colloids through packed beds. *Environ. Sci. Technol.* 40 (20), 6336–6340.
- Sang, W., Morales, V. L., Zhang, W., Stoof, C. R., Gao, B., Schatz, A. L., Zhang, Y., Steenhuis, T. S., 2013. Quantification of colloid retention and release by straining and energy minima in variably saturated porous media. *Environ. Sci. Technol.* 47 (15), 8256–8264.
- Seymour, M. B., Chen, G., Su, C., Li, Y., 2013. Transport and retention of colloids in porous media: Does shape really matter? *Environ. Sci. Technol.* 47 (15), 8391–8398.
- Tian, Y., Gao, B., Ziegler, K. J., 2011. High mobility of SDBS-dispersed single-walled carbon nanotubes in saturated and unsaturated porous media. *Journal of Hazardous Materials* 186 (2-3), 1766–1772.
- Tien, C., Payatakes, A., 1979. Advances in deep-bed filtration. *AIChE J.* 25, 737–759.
- Toride, N., Leij, F. J., van Genuchten, M. T., 1999. The CXTFIT Code for Estimating Transport Parameters from Laboratory of Field Tracer Experiments, Version 2.1, Research Report No. 137. U.S. Salinity Laboratory, USDA, ARS, Riverside, CA.
- Torkzaban, S., Bradford, S. A., van Genuchten, M. T., Walker, S. L., 2008. Colloid transport in unsaturated porous media: The role of water content and ionic strength on particle straining. *J. Contam. Hydrol.* 96 (1-4), 113–127.
- Wan, J., Tokunaga, T. K., 1997. Film straining of colloids in unsaturated porous media: Conceptual model and experimental testing. *Environ. Sci. Technol.* 31 (8), 2413–2420.

- Weiss, T. H., Mills, A. L., Hornberger, G. M., Herman, J., 1995. Effect of bacterial-cell shape on transport of bacteria in porous-media. *Environ. Sci. Technol.* 29 (7), 1737–1740.
- Wu, L., Gao, B., Tian, Y., Munoz-Carpena, R., Zigler, K. J., 2013. DLVO Interactions of Carbon Nanotubes with Isotropic Planar Surfaces. *Langmuir* 29 (12), 3976–3988.
- Xu, S., Liao, Q., Saiers, J. E., 2008. Straining of nonspherical colloids in saturated porous media. *Environ. Sci. Technol.* 42 (3), 771–778.
- Yao, K.-M., Habibian, M. T., O’Melia, C. R., 1971. Water and waste water filtration: Concepts and applications. *Environ. Sci. Technol.* 5, 1105–1106.
- Yau, K., Wang, K., Lee, A., 2003. Zero-inflated negative binomial mixed regression modeling of over-dispersed count data with extra zeros. *Biometrical J.* 45 (4), 437–452.
- Zeileis, A., Kleiber, C., Jackman, S., 2008. Regression models for count data in R. *Journal of Statistical Software* 27 (8), 1–25.
- Zuur, A., Leno, E., Walker, N., Saveliev, A., Smith, G., 2009. *Mixed Effects Models and Extensions in Ecology with R. Statistics for Biology and Health.* Springer, New York, NY.

Table 1: Selected properties of polystyrene colloids and silica sand.

Particle Properties	— Polystyrene Colloids —		
	Sphere	Barrel	Silica Sand
Radius r (μm)	0.5	na ^a	125-213
Surface-area equivalent effective radius r_{eff} (μm)	na	0.54	na
Minor semi-axis c (μm)	na	0.39	na
Major semi-axis a (μm)	na	0.67	na
Surface area (μm^2) ^b	3.14	3.65	$2.5\text{-}5.8 \times 10^5$
Ellipticity e (—) ^c	na	0.82	na
Electrophoretic mobility, ^d DI water, pH 7 ($\mu\text{m/s}$)/(V/cm)	-2.11 ± 0.05	-1.11 ± 0.84	-4.20 ± 0.03
Electrophoretic mobility, ^d high IS ^e , pH 10 ($\mu\text{m/s}$)/(V/cm)	-3.10 ± 0.00	-3.01 ± 0.26	-4.50 ± 0.02
ζ -potential, ^f DI water, pH 7 (mV)	-27.1 ± 0.6	-26.3 ± 3.1	-53.5 ± 0.0
ζ -potential, ^f high IS, pH 10 (mV)	-39.8 ± 0.0	-38.6 ± 3.4	-57.2 ± 0.0

^a na: not available or not applicable.

^b Surface area was calculated based on geometric parameters, r for spherical colloids and sand grains, a and b for barrel shaped colloids. Surface area is for a single particle.

^c $e = \sqrt{(a^2 - b^2)/a^2}$

^d Measured with a ZetaSizer 3000HSa (Malvern Instruments Ltd., Malvern, UK)

^e 100 mM NaCl solution buffered to pH 10 with 1.67 mM NaHCO₃ and 1.67 mM Na₂CO₃; total ionic strength was 106 mM.

^f Obtained from measured electrophoretic mobilities using the von Smoluchowski equation (Hiemenz and Rajagopalan, 1997).

Table 2: Experimental conditions, modeled data obtained from CXTFIT, and experimental mass balances.

experiment	rep	Measured Data				Modeled Data			Colloid Mass Balance		
		S_e (-)	θ_v (cm ³ /cm ³)	v (cm/min)	ψ (hPa)	v (cm/min)	D (cm ² /min)	λ (cm)	BTC (%)	Released (%)	Recovered (%)
barrel shape											
A	1	1.00±0.00	0.35±0.00	7.2±0.0	-0.8±0.4	6.7±0.1	3.2±0.6	0.48	8.1	15.3	23.5
	2					7.0±0.1	2.1±0.4	0.29	6.8	11.5	18.3
B	1	0.46±0.11	0.18±0.04	1.2±0.3	-32.2±1.6	1.0±0.0	1.4±0.3	1.35	0.0	4.7	4.7
	2					0.8±0.0	4.1±0.4	4.81	0.0	8.2	8.2
C	1	0.31±0.11	0.13±0.05	0.5±0.2	-29.2±1.3	0.5±0.0	0.6±0.1	1.20	0.0	14.6	14.6
	2					0.4±0.0	0.6±0.1	1.37	0.0	9.0	9.0
spherical shape											
D	1	1.00±0.00	0.35±0.00	7.2±0.0	-2.4±0.6	6.3±0.1	2.1±0.4	0.34	18.9	2.1	21.0
	2					6.3±0.1	1.8±0.3	0.29	21.5	2.2	23.7
E	1	0.44±0.13	0.17±0.05	1.2±0.4	-28.6±1.7	1.0±0.0	1.7±0.3	1.66	2.4	3.8	6.2
	2					1.0±0.0	1.5±0.3	1.46	1.5	3.9	5.4
F	1	0.31±0.05	0.13±0.02	0.5±0.1	-31.7±2.0	0.5±0.0	0.8±0.2	1.54	0.0	3.4	3.4
	2					0.5±0.0	0.6±0.1	1.40	0.0	3.4	3.4

Abbreviations:: rep: repetition; S_e : effective water saturation ($S_e = (\theta_v - \theta_r)/(\theta_s - \theta_r)$); θ_v : volumetric water content; θ_s : saturated water content; θ_r : residual water content; v : pore water velocity; ψ : matric potential; D : Dispersion coefficient; λ : dispersivity; BTC: mass balance breakthrough curve.

Table 3: Sequence of liquids used in colloid experiments.

Phase	Pore Volumes	Description
1	2	nano pure water initialize column for tracer breakthrough curve
2	4	1 mM NaNO₃ tracer breakthrough curve
3	2	nano pure water flush out tracer
4	2	1.67 mM NaHCO₃, 1.67 mM Na₂CO₃, 100 mM NaCl initialize column for colloid breakthrough curves
5	4	1.67 mM NaHCO₃, 1.67 mM Na₂CO₃, 100 mM NaCl, colloids colloid breakthrough curve
6	5	1.67 mM NaHCO₃, 1.67 mM Na₂CO₃, 100 mM NaCl flush out colloids
7	10	nano pure water release colloids from secondary energy minimum

Table 4: Results from the zero-inflated negative binomial model (ZINB) with *theta* being the dispersion parameter of the distribution given in values of the common logarithm. The standard combination for these analyses is for the barrels in depth $z = 0$ and a water content of $S_e = 0.31$.

Factor	Estimate	Std.-Error	z-value
Count Model Coefficients			
(Intercept)	4.81	0.29	16.29†
shape _{SPHERES}	0.42	0.23	1.80
watercontent	-1.27	0.38	-3.35†
depth	-0.72	0.07	-10.88†
shape _{SPHERES} :depth	0.29	0.05	5.46†
watercontent:depth	0.45	0.07	6.46†
Log(theta)	-0.23	0.14	-1.68
Zero-Inflation Model Coefficients			
(Intercept)	-1.46	0.35	-4.22†
shape _{SPHERES}	-1.55	0.51	-3.01†
depth	0.17	0.06	2.99†

†: significant at the level $\alpha = 0.01$

Table 5: Results from the logistic models for colloid deposition attributes. Colloid count was transformed using natural logarithm to improve normal distribution in the clustering model.

Factor	Estimate	Std.-Error	t-value
Clustering			
(Intercept)	-0.65	1.05	-0.621
ln(count)	0.08	0.22	0.36
depth	-0.32	0.09	-3.74†
watercontent	4.93	2.29	2.14*
watercontent ²	-5.38	1.71	-3.14†
depth:watercontent	0.33	0.10	3.43†
ln(count):watercontent	0.65	0.26	2.55*
Convex			
(Intercept)	0.24	0.32	0.74
shape _{SPHERES}	-1.62	0.25	-6.50†
watercontent	-1.07	0.40	-2.71†
Concave			
(Intercept)	-1.93	0.74	-2.63*
shape _{SPHERES}	2.18	0.84	2.60*
watercontent	2.39	0.93	2.57*
shape _{SPHERES} :watercontent	-2.70	1.06	-2.54*

*: significant at the level $\alpha = 0.05$; †: significant at the level $\alpha = 0.01$

Figure 1: Scanning Electron Microscopy images of spherical colloids (A), barrel shaped colloids (B), and sand grains (C). For every shape, water content, and sampling depth an overview image of several sand grains was taken and five grains were randomly chosen and magnified (C,D). On the magnified grain, three areas were randomly chosen (D), two of them are shown in subfigures E and F. Colloids were counted and clustering, surface roughness, as well as topography attributes were determined (E+F). Examples of smooth and rough surfaces on a sand grain (G), and of flat, convex, and concave topography (H).

Figure 2: Total DLVO interaction energy ΔG_{TOT} for the colloids interaction with the solid-water interface at ionic strength of $IS = 106 \text{ mM}$. (A) primary energy barrier, (B) magnification of secondary energy minimum.

Figure 3: Breakthrough and release curves from barrel shaped (A–C) and spherical colloids (D–F).

Figure 4: Depth profiles of barrel-shaped (A–C) and spherical colloids (D–F). SEM count data are in black shown as box plots, normalized concentrations (N_c : number of colloids in batch; N_{tc} : number of introduced colloids into column) per mass of dry sand measured by batch extraction are shown as blue lines. The Pearson correlation between the SEM mean count data and the concentration measurements was 0.57.