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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.

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 retention of

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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 presence 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 anon-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, die 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 m and 425 m 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 Sjostrom(2010). The packed medium had a porosity of $\varepsilon = 0.35$ cm^3/cm^3 and a bulk density of $\rho_b = 1.72$ 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 μm 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 μm (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