## Titanium dioxide nanoparticle simulation with LB-Colloids

### 4.1 Introduction to titanium dioxide simulation

1. Describe the importance of titanium transport
2. Describe background research on titanium transport (expand on these parts!)

Titanium dioxide nanoparticles are commonly used in consumer products such as toothpaste, sunblock, lotions, and house paints. Titanium dioxide based sunscreens can enter the environment directly by being washed off during swimming or other outdoor activities. Weathering of house paints and industrial materials creates another non-point source release mechanism for TiO2 into the environment. A case study of municipal wastewater treatment systems shows a large proportion of these particles are removed in the treatment process. The same study points out that a significant concentration of TiO2 nanoparticles are released through point source wastewater releases from tertiary treatment systems (*Kiser and others, 2009*). Further complicating the matter, application of bio-solids removed from wastewater treatment provides a non-point source vector for the release and transport of nanomaterials in much greater concentration through the soil environment (*Weir and others, 2012*).

A challenge for modeling nanoparticle transport is uniquely manufactured shapes such as rods and pyramids. Traditional colloid transport equations may not be able to adequately represent nanoparticle stability, transport and immobilization. Pore scale modeling however, may be able to bridge gaps in our knowledge of nanomaterial transport and allow for more accurate forecasting and prediction. Due to potential transformations, irregular shapes, and hetero-aggregation with other microscale particles calibration of nanomaterial transport may be necessary to model transport through the pore scale environment.

1. Describe the research problem
2. Brief overview of the project approach

Titanium nanoparticle transport is investigated with this study using D2Q9 lattice Boltzmann based colloid particle tracking code called LB-Colloids. Two-dimensional, nine fluid node lattice Boltzmann was used for computational efficiency and to develop a practical methodology for pore scale colloid transport modeling. Titanium dioxide nanoparticle breakthrough studies were performed by *Wang and Brusseau (written communication, 2017)* through packed sand beds. Pore scale modeling attempts to simulate the macroscopic breakthrough profiles of TiO2 nanoparticles in an effort to gain insight into transport, immobilization mechanisms, and provide a tool for making predictions with changes in environmental conditions. Results from forward models and calibrated models are presented in this chapter.

### 4.2 Laboratory methods

Laboratory nanoparticle breakthrough profiles were taken using a 5.08 cm long packed quartz sand bed. Quartz sand particles displayed a median grain diameter of 0.7 mm. Quartz sand was packed to 1.66 g/cm3 bulk density. Porosity was estimated as 0.375 based on a particle density of 2.65 g/cm3. The packed bed transport study was performed using a 0.3 mM phosphate-buffered saline with a constant outflow rate of 0.6 mL/min, which corresponded to a Darcy velocity of 1.83e-05 m/s. Titanium dioxide colloids were introduced into the system continuously at a concentration of 100 mg/L for approximately 13 pore volumes of elution. The experiment continued to run for approximately 31 pore volumes of elution to generate a titanium nanoparticle break though profile (Figure xxx).

### 4.2 LB-Colloid simulations

LB-Colloids, a simulation software that applies lattice Boltzmann computational fluid dynamics to a binarized dataset and includes additional colloid transport equations to simulate the transport and immobilization of colloid sized particles, was used for this study. A complete LB-Colloids simulation consists of two steps – 1) A lattice Boltzmann model is run until steady-steady state has been achieved 2) outputs from the steady-state lattice Boltzmann simulation are used as the input fluid domain and a colloid model is run. The benefit of the modular, two-step approach, is that transient state simulations can be added to this framework with the extension of the base LB-Colloid code and a method to save transient fluid domains from computational fluid dynamic models. The colloid particle tracking code base is also not limited to using lattice Boltzmann fluid domains. The only requirements needed are a fluid domain of velocity vectors and a binarized model domain.

“Virtual” TiO2 nanoparticles were simulated in this study. Nanoparticles are represented by their zeta potential, bulk density, and radius; nanoparticles are assumed to be spherical in these simulations, however in the natural environment nanomaterials and colloids encompass many shapes (both natural and engineered). Adjustments to the defining physical and chemical parameters of a colloid during calibration can assist in simulating non-spherical shapes.

#### 4.2.1 Spatial and Temporal Discretization

Synthetic porous media were generated using PSHPERE (discussed previously) at 200 pixels by 200 pixels which corresponds to 40,000 nodes. A discretization of 1 micron per pixel was used which corresponds to a domain size of 0.20 mm by 0.20 mm. Each porous media was generated to 0.37 +- 0.01 porosity. A grid refinement factor of 10 was applied to each porous media, for colloid simulations, bringing the total number of nodes to 4,000,000. A final discretization of 0.1 micron per pixel was used to simulate colloid transport within the fluid domain. The finer discretization allows for a more accurate representation of colloid-surface interactions than using the 1-micron lattice Boltzmann discretization.

For all simulations 1,000 non-dimensional time steps were performed to reach steady state with lattice Boltzmann. Dimensionalization of each set of simulation results through the non-dimensional Reynolds number allows for the time discretization between lattice Boltzmann computational fluid dynamics and the colloid transport equations. Each secondary colloid simulation was simulated for 22,000,000 time steps at a time discretization of 1e-6 seconds per time step for a total of 22 seconds. 22 seconds corresponds to approximately 2 pore volumes of elution from these porous media. Two pore volumes of elution was chosen to capture the breakthrough profile of TiO2 nanoparticles recorded in the laboratory. Longer simulations to match the complete laboratory profile are possible, however the computational time would be much longer and better suited for prediction modeling instead of the inverse modeling approach taken in this study.

#### 4.2.2 Porous Medium Boundary conditions

Porous media was randomly generated as a binary array in which each value (0, 1) represents a distinct phase (solid, pore space). Porosity for each porous media was specified to be 0.37 +- 0.01 to correspond with laboratory reported porosity. The specific grain radius for each simulation was specified as 1.7e-5 m. This grain radius, is 0.1 times the laboratory grain radius. However, due to the two-dimensional assumption of the lattice Boltzmann colloid models, the smaller grain radius produced surface areas that are similar to those reported from the laboratory study (table of porous media properties).

#### 4.2.3 Lattice Boltzmann Boundary conditions

Lattice Boltzmann simulations were performed on each randomly generated porous media. No flow boundary conditions were added to the fluid domain boundaries in the x-principal direction. A periodic boundary condition was applied to the fluid domain boundaries in the y-principal direction. Five fluid boundary layers were applied to the top and bottom of the lattice Boltzmann simulation. Addition of these boundary layers prevents localized velocity maximums from occurring at the inflow boundary of the porous media due to the velocity distribution of outflow. No slip and bounce back boundary conditions were applied at pore-solid interfaces within the fluid domain as described in previous sections.

Each lattice Boltzmann fluid simulation was parameterized with a number of constants. A non-dimensional fluid density of 1.0 was held constant as an initial condition for all simulations. The relaxation time parameter (non-dimensional) was also held constant at 1.0 for all simulations. As stated previously, relaxation time values which deviate from 1.0 can cause numeric instability due to simple bounce back boundary conditions. A body force was applied to each simulation, with an initial estimate of 0.001, and calibrated until the simulation darcy velocity was within a specified tolerance of laboratory conditions. More discussion on this process is covered in the section titled Calibration.

#### 4.2.4 Colloid transport Boundary conditions

Titanium nanoparticle, porous media, and fluid physical and chemical properties were specified for each simulation. Nanoparticle simulations were parameterized using laboratory data and assumptions from literature. Simulated zeta potentials for quartz sand and titanium dioxide nanoparticles were taken from laboratory measurements (-51.2 and -42 mV respectively). Fluid ionic strength was simulated with the laboratory supplied value of 0.3 mM NaCl. Titanium dioxide nanoparticles were assumed to have a bulk density of 3800 Kg/m3 (reference) which equates to a colloid mass of 2.8e-10 mg at a measured diameter of 260 nm. Initial parameterization of fluid ionic strength was specified at 3.0e-4 to match the laboratory experiment. Colloids were released in the first fluid layer of the domain at the rate of 2 colloids per 0.1 second for the duration of the simulation. This value was chosen to match the fluid concentration of colloids released into the experimental setup.

### 4.3 Calibration

A three-step inverse modeling approach was taken for TiO2 nanoparticle simulations. Porous media, lattice Boltzmann, colloid simulations were calibrated in series. Each calibration will be described in the following sections. An unweighted PHI of 1.0 was specified as the limit of acceptable error during calibration. If the calibration criteria failed at any point, calibration was restarted from the beginning.

#### 4.3.1 Porous media calibration

Porous media model domains were generated by applying a random Gaussian approach using PSHPERE. Porosity and grain size were specified as inputs and held constant. The Gaussian approach, however does not produce a domain that is consistent with the specified porosity. A simple algorithm was applied to regenerate the porous media if the domain is not within a specified tolerance (0.01 for this study). A secondary sweep line algorithm was applied to all model domains to ensure percolation. The third porous media calibration criteria was a mean pore diameter to colloid radius ratio greater than 70 (dimensionless).

#### 4.3.2 Lattice Boltzmann calibration

Steady state lattice Boltzmann simulations were performed on each of the synthetic porous media. Steady state simulations were calibrated to laboratory column darcy velocity by altering the applied simulation gradient. A gradient upgrade factor for calibration was calculated by

where was the target velocity and was the simulation’s darcy velocity. Application of this upgrade factor led to rapid convergence toward the target, often yielding a solution within three iterations. Simulation velocities were calibrated within a tolerance of +- 1.0e-06 m/s. (Add table of name, gravity, and darcy velocity).

#### 4.3.3 Colloid simulation calibration

Colloid particle tracking outputs were used to calculate the residual (PHI) and determine if a simulation was within the limit of acceptable error. Secondary calibration of colloid simulation ionic strength was performed using a random perturbation method. The slope of the phi was then calculated to determine the direction of ionic strength adjustment during calibration update iterations. XX simulations met the residual criteria and were used in this study (table of residuals, figure of 1:1 simulated vs. laboratory? With regression talk about these calibration results?). If the simulation did not meet residual criteria (PHI < 1.), it was automatically restarted from the beginning of the calibration process, by generating a new simulation domain.

### 4.3 Calibration Results

### 4.4 Discussion/Limitations

1. Talk about the limitations/advantages of this approach
2. Link CDE to a field-based approach if possible (maybe show a Hydrus1d run of colloid transport)

### 4.5 Conclusions

1. Conclude research with ‘Life’s a happy song’