The simulation of NZVI transport in saturated soil layer using trajectory analysis method

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Abstract

Suspended nano-scale particles are subject to some scavenging factors while they are migrating through porous media, which will diminish the practicability of deploying nano-scale iron in the groundwater aquifers. These factors include particle size, pH value, ion intensity, suspended liquid characteristics and groundwater velocity, etc. When particle size is much smaller than the pore size in saturated soil layer, the effect of Brownian Diffusion will become more significant for transport. This phenomenon is similar to the colloidal particles transporting through filter bed in industrial applications. Hence, in this study we are going to simulate the transport behavior of the nano-scale particles in groundwater by applying the same methodology as the simulation of colloid particle transport in porous media. The pore structure in soil layer is characterized by the constricted tube model. The absorbing situation of particles on soil surface is going to be determined by trajectory analysis in the constricted tube. Compared with the column experimental results, we could validate the simulation results. Moreover, by adjusting the parameters including Brownian and DLVO forces in calculation, we expect to find the better simulation results to predict the experimental results.

Keywords: NZVI, Nanoscale zero valent iron, transport model, trajectory analysis

1. Introduction

Direct injection of zero valent iron has been widely used in treating groundwater aquifers contaminated with chlorinated hydrocarbon. However, the efficiency decreases and the cost rises due to the poor spreading ability of iron particles in the subsurface environment. In recent years, the dispersing technology of particles has been widely discussed due to the development of nanoscale technology. Improving the stability of nanoscale particles has been extensively explored (Alessi and Li, 2001), it suggested that there is no direct relationship between transport and stability of colloid. Instead, interaction with soil and nanoscale particles makes great influence on transport. Hence, the critical steps of improving particle transport are to realize the relationships between particle stability, interactions with soil particles, and transports in soil media.

Implementing a model to predict the transport of nanoscale zero valent iron in the groundwater aquifers is valuable for evaluating the practicability of deploying nano-scale iron. In this study, the simulation of NZVI transport in groundwater was conducted by applying the same methodology as the simulation of colloid particle transport in porous media. The pore structure in soil layer was characterized by the constructed tube model. The absorbing situation of particles on soil surface was determined by trajectory analysis in the constricted tube.

2. Simulation of NZVI transport in saturated soil layer

2.1 The distribution of soil particles

To accurately simulate the transport behavior of the ZNVI in subsurface environment, we define collectors of soil particle in groundwater layer connected by network shown as in Figure 1. It was assumed that the average velocity in collectors is equal. Then we were able apply trajectory analysis, DLVO theory and Brownian movement to simulate the obstruction or absorbability of nanoscale particles in collectors. If particles were absorbed on the surface of a collector, the radius of the collector would increase. In other words, the aperture of collector will drop. The penetration ratio is calculated by the quantity of remaining particles. In addition, the trajectory analysis consisted of three sections including the distribution of fluid field, the balance between particles and the external force of particles.

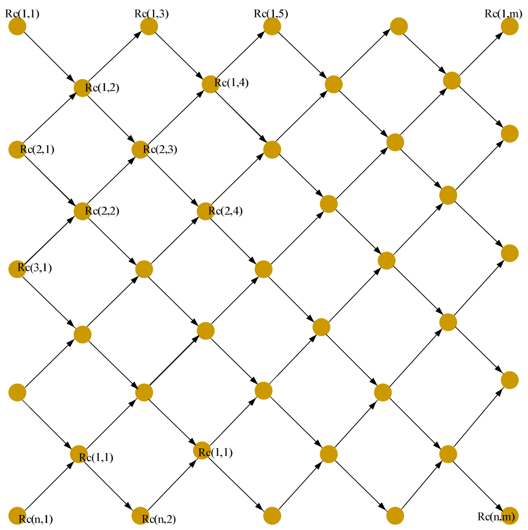

Figure 1. Diagram for distribution of simulation soil particles and particles route in the model

2.2 The distribution of flow field

In the present study, the flow field equations established by Chow and Soda (1972) were adopted. It was assumed that the filter bed is composed of a number of unit bed elements (UBEs) or collectors connected in series, The UBEs are uniform in thickness. Each UBE contains a number of parabolic constricted tube with a distribution of a given size. The schematic diagram for simulating the deposition of nanoscale particles in a constricted tube is shown in Figure 2.

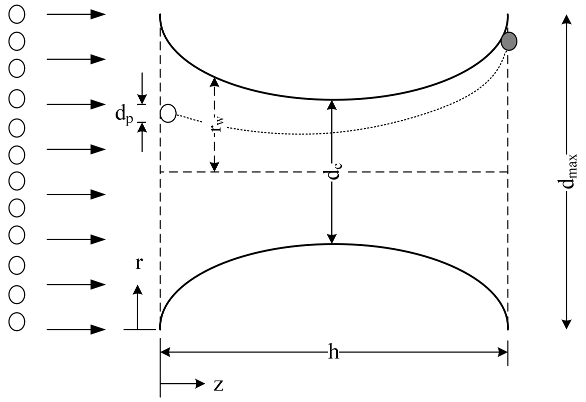

Figure 2. The schematic diagram for simulating the deposition of nanoscale particles in a constricted tube

For a spherical collector with diameter (d_f), the relationship between the smallest radius (r_c), the maximum radius ($r_{\max}$), the radial radius (r_w), the length of constricted tube (l_f), and the smallest diameter (d_c) are defined as (Choe, 2000) :

$$r_c = \frac{d_c}{2} = 0.175 d_f \tag{1}$$

$$r_{max} = \frac{d_{max}}{2} = \frac{1}{2}\left[\frac{\varepsilon(1-S_{wi})}{1-\varepsilon}\right]^{1/3} d_f \tag{2}$$

$$r_w = r_c + 4(r_{max} - r_c)\left(0.5 - \frac{z}{l_f}\right)^2 \tag{3}$$

$$l_f = \left[\frac{\pi}{6(1-\varepsilon)}\right]^{1/3} d_f \tag{4}$$

where S_{wi}: fraction of saturation; ε: soil porosity; z: axial distance of particle

The distribution of flow field is always described by the stream function (ψ) that can be expressed as:

$$E^4\psi = 0 \tag{5}$$

where

$$u_r \text{ (axial velocity)} = \frac{1}{r}\frac{\partial\psi}{\partial z} \tag{6}$$

$$u_z \text{ (radial velocity)} = -\frac{1}{r}\frac{\partial\psi}{\partial r} \tag{7}$$

$$E^2 = \frac{\partial^2}{\partial r^2} - \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2} \tag{8}$$

When the flow velocity is zero on the collector surface and reaches its peak (using peak instead of maximum) in collector center, the bounded conditions are,

If $r = r_w$, $u_r = u_z = 0$

If $r = 0$, $\frac{\partial u_z}{\partial r} = 0$ and $u_r = 0$

The expressions of the velocity components u_r and u_z are

$$u_r = u_m\left(u_{ro} + R_m u_{r1} + {R_m}^2 u_{r2}\right)\frac{{r_m}^2}{r_w l_f} \tag{9}$$

$$u_z = u_m\left(u_{zo} + R_m u_{z1} + {R_m}^2 u_{z2}\right)\frac{{r_m}^2}{{r_w}^2} \tag{10}$$

and

$$u_{r0} = -2\frac{dR_w/dZ}{R_w}(R^3 - R) \tag{11}$$

$$u_{r1} = \frac{0.25}{R} N_{Re,m}\left\{F\left[\frac{\frac{d^2R_w}{dZ^2}}{R_w} - \left(\frac{\frac{dR_w}{dZ}}{R_w}\right)^2\right] + \frac{dF}{dZ}\frac{\frac{dR_w}{dZ}}{R_w}\right\} \tag{12}$$

$$u_{r2} = -0.5\left\{\left(9\frac{dR_w}{dZ}\frac{d^2R_w}{dZ^2} - R_w\frac{d^3R_w}{dZ^3}\right)\frac{G}{R} + \left[5\left(\frac{dR_w}{dZ}\right)^2 - R_w\frac{d^2R_w}{dZ^2}\right]\frac{dG}{RdZ}\right\} - 0.125N_{Re,m}\left\{2\frac{dR_w/dZ}{R_w}\left[\frac{d^2R_w/dZ^2}{R_w} - \left(\frac{dR_w/dZ}{R_w}\right)^2\right]\frac{E}{R} + \left(\frac{dR_w/dZ}{R_w}\right)^2\frac{dE}{RdZ}\right\} \quad (13)$$

$$u_{Z0} = 2(1-R^2) \quad (14)$$

$$u_{z1} = -\frac{0.25}{R}N_{Re,m}F\frac{dF}{dR}\frac{dR_w/dZ}{R_w} \quad (15)$$

$$u_{z2} = 0.5\left[5\left(\frac{dR_w}{dZ}\right)^2 - R_w\frac{d^2R_w}{dZ^2}\right]\frac{dG}{RdR} + 0.125N_{Re,m}\left(\frac{dR_w/dZ}{R_w}\right)^2\frac{dE}{RdR} \quad (16)$$

where

r_m: average radius of constriction tube (cm), defined as

$$r_m = \frac{1}{l_f}\int_0^{l_f} r_w\, dz$$

Z: dimensionless particle distance along axial direction of constriction tube, defined as $Z = z/l$

R: dimensionless r distance along radius direction of constriction tube, defined as $R = r/r_w$

R_w: dimensionless distance with constriction tube wall to axle center, defined as $R_w = r_w/r_m$

R_m: dimensionless average radius of constriction tube, defined as $R_m = r_m / l_f$

$N_{Re,m}$: Reynolds number, defined as $N_{Re,m} = u_m r_m \rho_f/\mu$

$F = (R^8 - 6R^6 + 9R^4 - 4R^2)/9$

$G = (R^2-1)R^2/3$

$E = (32R^{12} + 305R^{10} + 750R^8 - 713R^6 + 236R^4)/3600$

2.3 The balance between particles (Langevin Eq.)

Several researches have used Langevin Eq. to describe the balance between particles in trajectory analysis. (Chang, 2004；Ramarao, 1994) Langevin Eq. is defined as:

$$m_p\frac{dV}{dt} = F_d + F_r + F_e \quad (17)$$

where

m_p: mass of particle (Fe^0) (g)

V: velocity vector of particle(cm/sec)

t: time (sec)

F_d: traction force of flow (dyne = g・cm/sec^2), defined as

$F_d = m_p\beta(U-V)$, where U is the velocity vector of flow (cm/sec) and β is the friction coefficient (sec^{-1})

F_r: repulsion force of freedom (dyne), defined as $F_r = m_pA(t)$, where $A(t)$ is Gaussian white noise process in stochastic terms (cm/sec^2)

F_e: external force (dyne), defined as $F_e = F_{vdW} + F_{elect}$

3. Simulation procedure

With consideration of the inertia term in the force balance equation and the flow fluid around the collector, the particle trajectory can be determined by integrating the Langevin equation as below.

The particle velocity vector is represented as:

$$V = V_0e^{-\beta t} + U(1-e^{-\beta t}) + R_v(t) + \frac{1}{\beta}\left(\frac{F_{vdW}+F_{elect}}{m_p}\right)(1-e^{-\beta t}) \quad (18)$$

Where

V_0: initial velocity of particles (cm/sec)

U: fluid velocity vector (cm/sec)

E_{elect} : force of electrostatic repulsion

E_{vdW} : force of van der Waals

β: friction coefficient per unit mass of particle (sec^{-1})

$$\beta = \frac{6\pi r_p\mu}{C_s m_p} \quad (19)$$

C_s : Revision factor of Cunningham

Substituting dS/dt for V with the initial condition S=S0 at t=0, the trajectory equation of particles can be expressed as:

$$S = S_0 + \left\{\frac{V_0}{\beta}(1-e^{-\beta t}) + U\left[t - \frac{1}{\beta}(1-e^{-\beta t})\right]\right\} + \left\{R_r(t) + \left(\frac{F_{vdW}+F_{elect}}{\beta m_p}\right)\left(t + \frac{e^{-\beta t}}{\beta} - \frac{1}{\beta}\right)\right\} \quad (20)$$

$R_r(t)$ is defined as a random deviate of displacement increment due to Brownian motion, which is bivariate Gaussian distribution (Chen, 2001).

R_{ri} is an approximate value of $R_r(t)$, defined as:

$$R_{ri} = n_i \times \frac{\sigma_{Vri}}{\sigma_{Vi}} + m_i \times \left(\frac{{\sigma_{ri}}^2 - {\sigma_{Vri}}^2}{{\sigma_{Vi}}^2}\right)^2 \quad (21)$$

n_i and m_i are the normally distributed numbers between 0 and 1.

$$\sigma_{Vi}{}^2 = \frac{\bar{q}}{\beta}\left(1 - e^{-2\beta\Delta t}\right) \quad (22)$$

$$\sigma_{ri}{}^2 = \frac{\bar{q}}{\beta^3}\left(2\beta\Delta t - 3 + 4e^{-\beta\Delta t} - e^{-2\beta\Delta t}\right) \quad (23)$$

$$\sigma_{Vri}{}^2 = \frac{\bar{q}}{\beta^2}\left(1 - e^{-\beta\Delta t}\right)^2 \quad (24)$$

where, $\bar{q} = \frac{\beta k_B T}{m_p}$

$$V_0(\text{initial velocity of particle}) = U_0 + V_0' \quad (25)$$

where

$V_0' = 0$

or

$$V_0' = \sqrt{\frac{3\beta k_B T}{m_p}}$$

The displacements were calculated by velocity along radius direction of constriction tube when analysis of particles absorb. The velocity is as following:

$$U = u_r(r,z) = u_m\left(u_{ro} + R_m u_{r1} + R_m{}^2 u_{r2}\right)\frac{r^2}{r_w l_f} \quad (26)$$

Retention time of particle in collector was calculated by displacement and velocity along axial direction of constriction tube as following. ΔZ was defined as 1/10Z.

$$u_z(r,z) = u_m\left(u_{zo} + R_m u_{z1} + R_m{}^2 u_{z2}\right)\frac{r_m{}^2}{r_w{}^2} \quad (27)$$

$$t = \frac{\Delta Z}{u_z} \quad (28)$$

It is important to determine the adsorbent of particles while calculating the absorbable trajectory of particles. In this study, adsorbent of a particle on collector was determined when the particle touches the collector. In addition, the particle could leave the collector when the distance between the center of particle and tube wall is longer than the length of collector.

The condition of collectors for obstruct is described by the filter coefficient (α), where α is a correctional value in the model. The condition of collectors for obstruct is defined as:

$$r_c \le \alpha r_p \quad (29)$$

At each time step, if the distance between the approaching particle and the pore wall is smaller than the diameter of the particle, then this particle is assigned as the "captured" particle. When a particle is captured in a bond of the network, the increase of radius of collector in that bond can be calculated by the following equation. When there are N particles captured in the bond, the new radius of the bond r_f can be related to the r_{f0} by Chan (2004):

$$\frac{1}{r_f{}^4} = \frac{1}{r_{f0}{}^4} + \frac{0.75}{r_f{}^4}\sum_{i=0}^{N}\frac{r_{pi}}{l_f}\left[1 - \left(1 - \frac{r_{pi}}{r_{f0}}\right)^2\right]^2 \cdot K_1 \quad (30)$$

where

r_f : the new radius of collector (cm)

r_{f0} : the initial radius of collector(cm)

r_{pi} : the radius of particle (cm)

$$K_1 = \frac{1 - \frac{2}{3}\left(\frac{r_p}{r_{f0}}\right)^2 - 0.20217\left(\frac{r_p}{r_{f0}}\right)^5}{1 - 2.105\left(\frac{r_p}{r_{f0}}\right) + 2.0865\left(\frac{r_p}{r_{f0}}\right)^3 - 1.7068\left(\frac{r_p}{r_{f0}}\right)^5 + 0.72603\left(\frac{r_p}{r_{f0}}\right)^6} \quad (31)$$

The simulation parameters are given in Table 1. Simulations were performed on a two-dimensional network (NL=60×60) at constant flow rate. The penetration ratio C/C0 could be derived from the Brownian trajectory analysis and the stochastic simulation procedure in different types of DLVO interaction energy curves. The particles were uniformly distributed in this study. A Fortran program is selected to calculate the simulation results.

Table 1. Parameter values adopted in the simulation

parameter	value	Ref.
c_p	2500 ppm	Measured
C_s	1.0	Chen, 2001
d_f	0.2 mm	Measured
d_p	100 nm	Measured
kB	1.38×10^{-16} erg/K	Chen, 2001
A	3×10^{-14}	Chen, 2005
$N_{Re,m}$	0.00167	Calculation
S_{wi}	0.127	Chen, 2001
T	293 K	Measured
Um	0.1 cm/min	Measured
ε_0	0.48	Measured
ρ_f	1.0025 g/cm^3	Calculation
ρ_g	7.82 g/cm^3	Measured
μ	1 cp	Chen, 2001
φ_C	-1.15 mV	Measured
φ_P	-47.8 mV	Measured
N_{elect}	18.126	Calculation
N_{E1}	70.3	Calculation
N_{E2}	0.169	Calculation

An overall description of the simulation procedure is presented in Figure. 3. Figure 4 is the diagram for simulating deposition of nanoscale particles by trajectory analysis in a constricted tube. By comparing with the available experimental data, the accuracy of the present simulation method will be discussed.

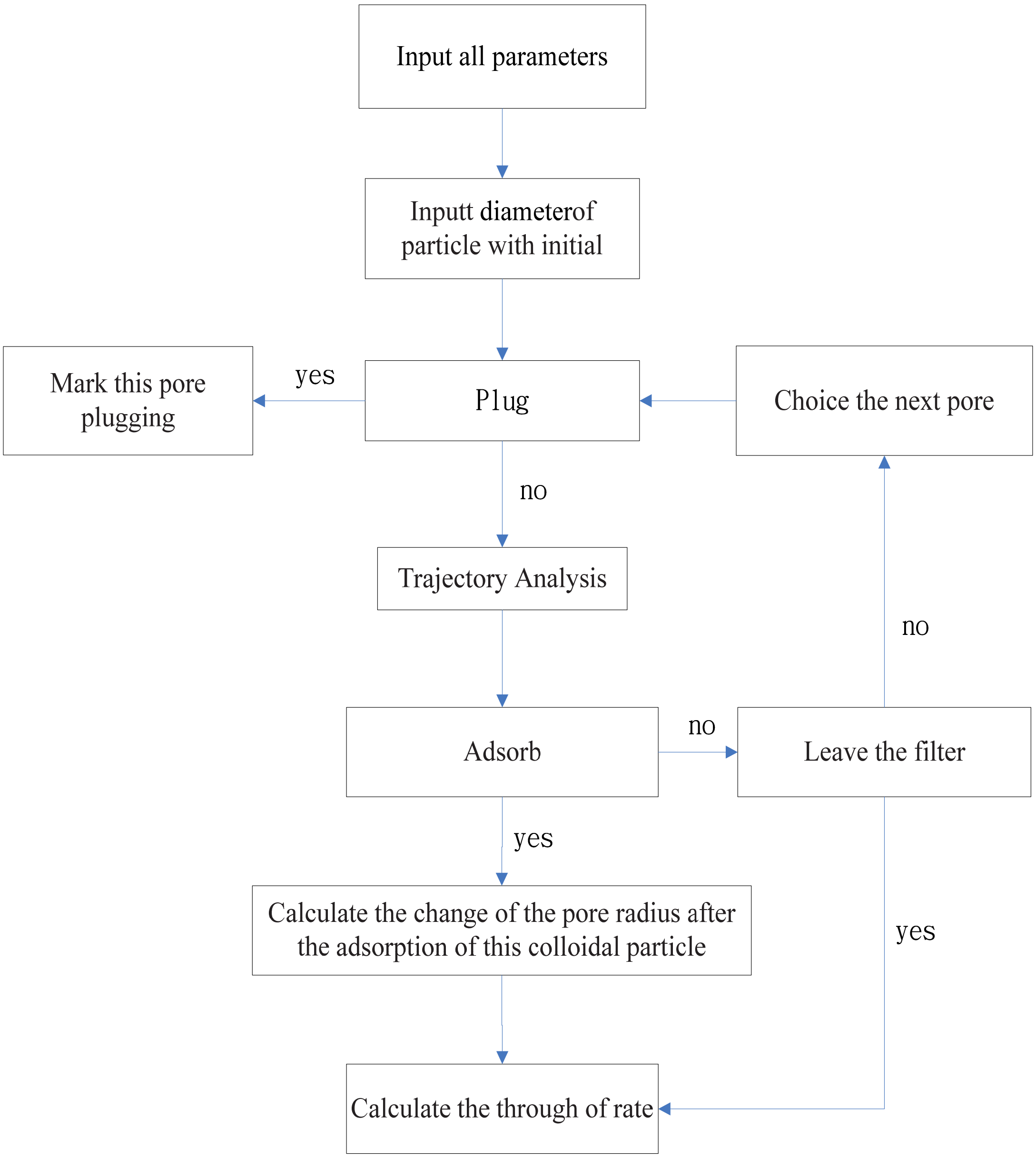

Figure 3 Flowchart of the model in this study

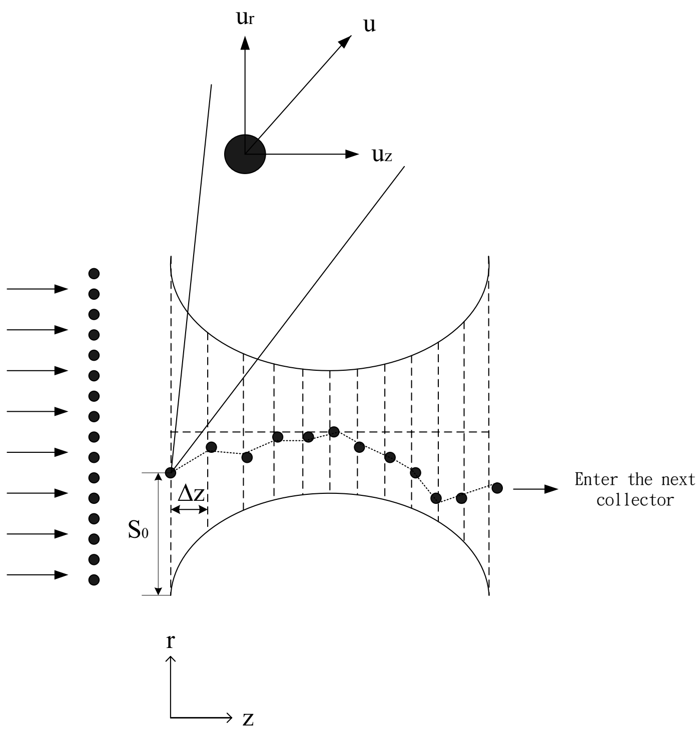

Figure 4 The diagram for simulating deposition of nanoscale particles of trajectory analysis in a constricted tube

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