Microscale Simulation of Nanoparticles Transport in Porous Media for Groundwater Remediation

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Abstract

Micro and Nanoscale zerovalent iron (MZVI and NZVI) is one of the most promising reagent for the remediation of contaminated groundwater; these particles, in fact, can efficiently degrade, through redox reactions, recalcitrant and carcinogenic compounds.

The aim of this study is to simulate at the microscale the transport of iron nanoparticles, their interaction with the porous media and their deposition on the aquifer material.

The simulations have been carried out with a Langrangian approach implemented in COMSOL Multiphysics 4.2a. The model under study includes the relevant forces acting on the single particles such as drag, Brownian, gravity, Van der Waals and electric double layer force.

The simulation results can deliver, thanks to this microscale description, an estimation of the attachement efficiency that can be used for macroscale simulations and compared with the relationships obtained by the clean bed filtration approach.

Keywords: Zerovalent iron, microscale, aquifer remediation, Lagrangian particle tracing.

1. Introduction

Micro and nanoparticles of zerovalent iron (MZVI and NZVI) are one of the most promising reagent for the remediation of contaminated groundwater [15].

These particles can degrade, through redox reactions, recalcitrant and carcinogenic compounds such as perchloroethylene and trichloroethylene.

Due to his very high specific surface NZVI is characterized by a high reactivity. Furthermore it can be injected in the subsurface more easily if compared to the emplacement of granular iron commonly used in permeable reactive barriers [3] and it can be used directly to treat the source of contamination itself and not only on the plume (the dissolve part of contamination).

The iron nanoparticles are normally injected into the soil as an aqueous slurry, which has to come into contact with the source of contamination or reach the polluted groundwater [10].

The main issue related to the field application of this technology is the reduced mobility of NZVI. In order to enhance the mobility of iron nanoparticles on the subsurface, it is important to (i) prevent the formation of large aggregates that tend to be easily filtered and (ii) reduce the attachment of nanoparticles to the soil grains. To date, the best strategy to achieve these goals has been to modify the surface of the iron nanoparticles using polymers or surfactants [10].

A number of other studies [12, 13] have investigated the MZVI and NZVI mobility using transport tests in order to develop a powerful

tools for the design and the implementation of full scale zerovalent iron applications [13].

The aim of this study is to simulate the transport of iron nanoparticles and their interaction with the porous media at the microscale.

The deposition of iron particles on the porous media is an important mechanism controlling the mobility of colloids in aquifer systems and the effectiveness of the technology. A microscale domain (few micron) was reconstructed through SEM images of a sandy aquifer material and the flow field was calculated using Navier-Stokes equations over a wide range of flow velocities, but always in laminar conditions.

In porous media the dynamic of the particles inside of a pore is governed mainly by drag, gravity and Brownian forces, but close to the sand surface also the electric double layer (EDL) and the Van der Waals forces (VdW) come into play and become prevailing. In order to simulate the trajectories of the MZVI and NZVI particles a Lagrangian approach was implemented by using the COMSOL *Particle Tracing for Fluid Flow* module.

The aim is to derive a correlation between the parameters characterizing the iron particles, the sand grains and the flow field and the capacity of MZVI and NZVI to cover long distance without be captured from the porous media grains.

This correlation would be useful for future application in field and for the project of a real reclamation activity.

2. Methods

2.1 Geometry and flow field

In a granular medium, the flow field around each grain is influenced by the neighbouring collectors and so studying the flow field around an isolated sphere could be not much representative. Therefore the first approach used to construct a computational domain is the Happel's geometry [6]. The Happel's sphere-in-cell model (Figure 1), in fact, simulates the flow interaction due to the presence of other particles through solve the fluid flow in a fluid shell around each solid grain considering that it's affected by the neighbouring grains.

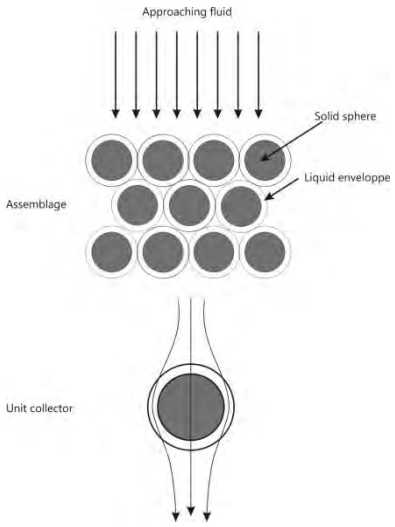

Figure 1: schematic description of Happel's sphere-in-cell flow model for a homogeneous porous media (adapted from [5]).

In the Happel's model, the porous medium is treated as an assemblage of identical, spherical collectors, each of which is enveloped by a shell of fluid. The thickness of the shell, *b*, is determined so that the overall porosity *n* of the

porous medium is maintained for the single collector of radius a_c [4]:

$$b = a_c(1-n)^{\frac{1}{3}} \qquad \text{eq.1}$$

In this case an analytic solution for the flow field exists and it is reported in literature (Elimelech M. [4], Chi Tien, B. V. Ramarao [9]) and represented in Figure 2.

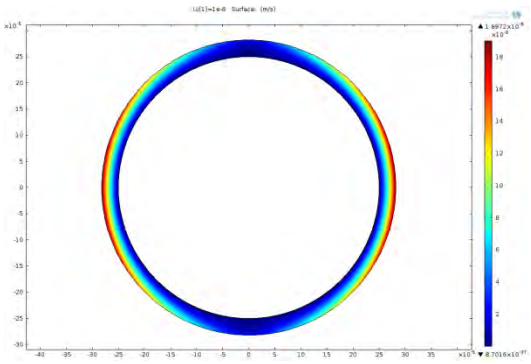

Figure 2: Flow field in Happel's model.
Grain radius a_c = 250 µm, porosity n = 0.30, approach velocity $U = 10^{-6}$ m/s.

The second step consists in considering a more realistic 2D domain. Starting from some sands samples, scanning electron microscope (SEM) was used in order to obtain some digital image of them (Figure 3).

Then, through a CAD manipulation, computational grids have been obtained and used in COMSOL Multiphysics 4.2a (Figure 4).

The domain has dimension of $2.69 \cdot 10^{-3}$ x $2.23 \cdot 10^{-3}$ m.

The flow field was found by solving the Navier-Stokes equations in laminar conditions, using the *Laminar flow* interface of COMSOL Multiphysics 4.2a.

With a parametric sweep, a range of approach velocity U between 10^{-6} m/s and 10^{-3} m/s has been investigated (Figure 5) and an *inlet velocity* equal to U, the approach velocity, has been imposed.

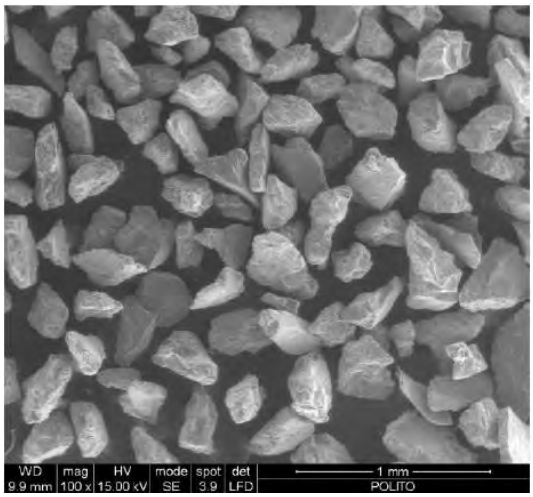

Figure 3: Original SEM photograph of a sandy porous media.

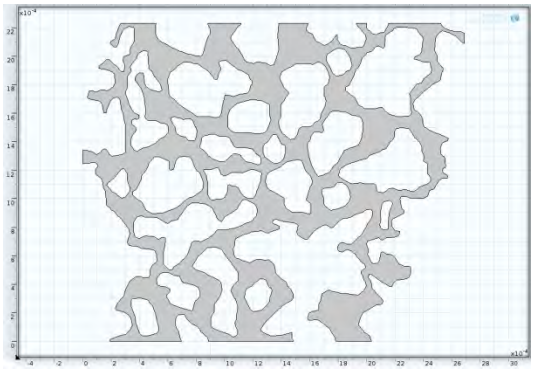

Figure 4: Definitive geometry used in COMSOL Multiphysics 4.2a.

The grains boundaries are all set as *wall*, so that the fluid velocity on their surface is zero.

On the rest of the boundary sites a *symmetry* boundary condition, that prescribes no penetration and vanishing shear stresses, was used.

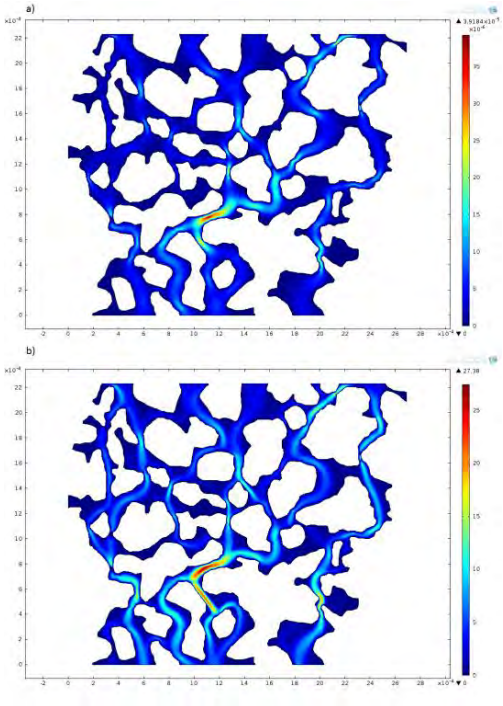

Figure 5 : Flow field in the 2D porous medium domain, a) approach velocity $U = 10^{-6}$ m/s, b) approach velocity $U = 1$ m/s.

2.2 Particle tracing

Particles transport was simulated by using a Lagrangian approach exploiting the *Particle Tracing for Fluid Flow* module.

The Lagrangian approach was chosen because it gives the possibility to describe accurately the particles trajectories in the flow field and their interaction with the sand grains at a microscale by implementing all the forces acting on them.

The basic equation of this approach is the classical Newton's low:

$$\sum_i F_i = m_p \frac{d\vec{U}}{dt} = \vec{F}_D + \vec{F}_G + \vec{F}_{EDL} + \vec{F}_{VdW} + \vec{F}_B \quad \text{eq.2}$$

Where $\vec{U}$ and m_p are the particle velocity and mass, $\vec{F}_D$ is the drag force, $\vec{F}_G$ the gravity force, $\vec{F}_{EDL}$ the Electric Double Layer force, $\vec{F}_{VdW}$ the Van der Waals force and $\vec{F}_B$ the Brownian force.

Their complete mathematical formulations are reported in Table 2. In Table 1 there are the constants and parameters numeric value used in the simulations.

The gravity force, is constant in all domain. Its direction is always vertical, perpendicular to the earth surface.

The drag force depends from the flow field, in general it is bigger in the centre of each pore and becomes less significant near the grains boundaries where the velocity of the flow fields is zero.

Water density	ρ_f	998 kg/m^3
Iron particles density	ρ_p	5500 kg/m^3
Dynamic viscosity	μ_f	$1\cdot10^{-3}$ Pa·s
Water electric permittivity	ε_{0r}	$7.0832\cdot10^{-10}$F/m
Invers of Debye parameter	k^{-1}	$3.2\cdot10^{8}$ 1/m
Hamaker constant	H	$1.51\cdot10^{-20}$ J
Gravity acceleration	g	9.81 m/s^2
Happel's collector radius	a_c	250 µm
Iron particles radius	a_p	40 nm,400 nm,4 µm
Boltzmann constant	K	$1.38065\cdot10^{-23}$ J/K
Absolute temperature	T	298 °K
Collector zeta potential	ξ_c	-7 mV
Iron particle zeta potential	ξ_p	-58 mV

Table 1: Constants and parameters used in the simulations.

Forces	Mathematical expression
Drag force	$\vec{F}_D = 6\pi\mu a_p(\vec{u}-\vec{v})$
Gravity force	$\vec{F}_G = \frac{4}{3}\pi a_p^3(\rho_p-\rho_f)\vec{g}$
Electric double layer force	$\vec{F}_{EDL} = \varepsilon_0\varepsilon_r a_p \frac{(\xi_p^2+\xi_c^2)\kappa e^{-\kappa h}}{2(1-e^{-2\kappa h})}\left[2\frac{\xi_p\xi_c}{(\xi_p^2+\xi_c^2)}-e^{-\kappa h}\right]\vec{n}$
Van der Waals force	$\vec{F}_{VdW} = -\frac{Ha_p}{6h^2}\frac{\lambda(\lambda+28h)}{(\lambda+14h)^2}\vec{n}$
Brownian force	$F_B = R\sqrt{\frac{2\xi kT}{\Delta t}}$

The parameters (see also Table 1) are: *u* fluid velocity, *v* particle velocity, a_p particle radius, ρ_p particle density, ρ_f fluid density, *g* acceleration of gravity, *H* Hamaker constant, *h* particle – collector distance, λ average wavelength of electron oscillation (100 nm), *R* random normal distribution number, *k* Boltzman's constant, *T* absolute temperature, ξ friction coefficient (equal to $6\pi\mu a_p$), *k* Debye - Huckel parameter, ξ_P iron particle zeta potential, ξ_C collector zeta potential

Table 2: Mathematical Expression of all forces considered in the Particle Tracing for fluid flow module.

F_{VdW} is the Van der Waals force, it's an attractive force between particles and aquifer grains. It is due to the dipole moments generated from the temporary asymmetry of the electrons cloud distribution around the nucleus of atoms. It is always negative.

F_{EDL} is the electric double layer force: the particles and the collectors (the aquifer grains) are provided with a surface charge which is balanced by ions presented in the solution creating so an electric double layer. It depends from both particle and grains zeta potential (a measured of the surface charge of them), from the water pH and from the water ionic strength. These two forces are active in all domain but significant only in a nanoscale range of distance between particle and sand grains, far away they quickly tends to zero.

The Brownian force is a random force and so its implementation requires the generation of a random number. Its formulation includes also some functions that take in consideration the presence of the solid walls [8]. These function are described by Elimelech (1995) [5].

Being the Brownian force a stochastic term, its explicit formula depends also on the time step

used by the software in order to solve the problem.

The particle tracing equations were solved by a time dependent solver and the time step, automatically chosen by the software, is used in the force formulation.

The time step, however, must be greater than the particle momentum relaxation time $MRT = m_p/\xi$, where m_p is the particle mass and ξ friction coefficient (equal to $6\pi\mu a_p$) [8].

This sets the lower limit, but it is necessary also to consider a higher limit to assume the forces constant in that time step.

The largest force gradients are present near the grains surface, where the distance between grains and NZVI particles became small and the F_{VdW} and F_{EDL} could have big oscillations.

Since in COMSOL we can use only a single time step for the whole domain, without refining it in these regions, we were obliged to use in all domain a very small time step in order to have a very small particle displacement (1-2 nm) able to feel the high gradient of forces.

This is a very critical point because the computational time significantly increases, therefore a limited number of particles can be simulated.

2.3 Collector efficiency

The mechanisms leading to colloid deposition can be divided into two steps: transport and deposition. The term "transport" refers to the mechanisms that bring the colloidal particles from the bulk of the fluid to the proximity of the grain surface. These mechanisms (Figure 6) are interception (when the streamline along which the particle is moving crosses a sand grain), gravitational sedimentation (due to the settling of the particles when their density is higher than water's), and Brownian diffusion (when Brownian thermal movement diverge particles from a streamline and brings them to the grain surface) [11].

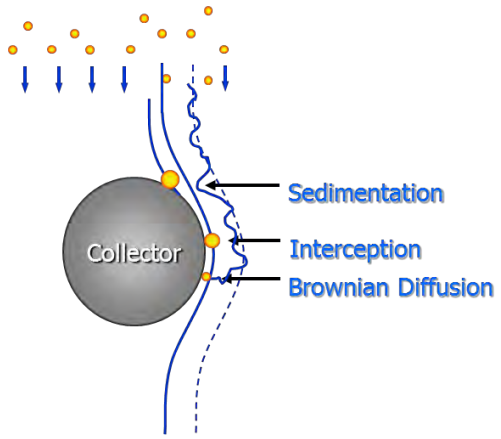

Figure 6: Different mechanisms of particle adhesion to the grain.

Conversely, the properly called "attachment" step is controlled by surface interaction forces.

According to the CFT theory, the transport step is described by the single-collector contact efficiency η_0, while the attachment step is defined by the attachment efficiency α.

Many equations have been proposed to date for the single collector efficiency [Rajagopalan and Tien, 1976; Tufenkji and Elimelech, 2004]. The most complete one [Tufenkji and Elimelech, 2004] accounts for the superposition of the effects of hydrodynamic forces, van der Waals interactions and gravity effects, and proposes the following correlation equation [11]:

$$\eta_0 = 2.4 A_s^{1/3} N_R^{-0.081} N_{Pe}^{-0.715} N_{vdW}^{0.052} + 0.55 A_s N_R^{1.675} N_A^{0.125} + 0.22 N_R^{-0.24} N_G^{1.11} N_{vdW}^{0.053}$$

eq.3

where A_S is a porosity-dependent parameter, N_R is the aspect ratio, N_{Pe} is the Peclet number, N_{vdW} is the Van der Waals number (describing the entity of the Van der Waals interaction energy with respect to the thermal energy of the system), N_A is the attraction number (characterizing the effects of fluid velocity and Van der Waals interaction on the particle deposition due to interception), N_G is the gravity number (representing the ratio between the Stokes particle settling velocity to the effective velocity of the pore water). These are non-dimensional parameters. For more information see [14].

In eq.3 the first term represents the effects of diffusion, the second one the contribution due to interception, the third one the gravity effects.

3. Results

Both the geometries introduced above have been used in the simulations.

The approach velocity U was varied in order to simulate different flow field and also the particle radius a_p was modified between different simulations (see Table 1).

All the forces listed in Table 2 has been implemented.

So, with respect to the work of Tufenkji and Elimelech, we consider also the effect of the electric double layer and the Brownian motion.

The collector efficiency is calculated as the ratio between the number of particles captured by the central grains and all the released particles.

In the Happel's model the particle release was from the top semicircle.

Different simulations increasing each time the number of particles released have been done.

For the cases with particle radius equal to 4 μm and 400 nm, simulations with 20, 100, 500, 1000 and 2000 particles were performed. For the smaller particles (40 nm of radius) only simulations with 20, 100, 150 and 200 particles have been performed.

Decreasing the radius of the particles, in fact, the particle mass decreases and the role of the Brownian force increases. It is therefore necessary to reduce considerably the time step of calculation, but this increases a lot the computational efforts, not allowing a significant number of particles release.

In the second geometry (that taken from the porous media image) the particles were released from a line in the top of the domain. In this case the particle trajectories calculation results to be problematic. The complexity of the geometry and of the flow field, in fact, increases a lot the computational efforts, limiting the numbers of particles for which is possible to plot a complete trajectory.

In order to calculate the collector efficiency in COMSOL we can use the *global evaluation* tool to evaluate the total number of particles released and the number of particles that exit from the domain. The difference gives us the number of particles captured by the grains. This number divided by the total number of particles released is the collector efficiency η.

As a general observation, the trajectory is much more vertical for the bigger particles that are heavier and that are so less mobile.

Furthermore, the smaller particles have trajectories more similar to the streamlines and we can also observe the Brownian vibration.

The flow field velocity also has an influence on the particles mobility.

The simulations carried out in the Happel's domain can be summarized in terms of collector efficiency, as showed in Table 3.

In the realistic domain instead, it was not possible to track a significant number of particles because of computational limits. So we were not able to calculate reliable statistics.

COLLECTOR EFFICIENCY η [%]			
	MZVI and NZVI particle radius [m]		
Velocity field [m/s]	$a_p = 4 \cdot 10^{-6}$	$a_p = 4 \cdot 10^{-7}$	$a_p = 4 \cdot 10^{-8}$
$U = 10^{-6}$	71	46	59
$U = 10^{-5}$	66	19	19
$U = 10^{-4}$	42	8	10
$U = 10^{-3}$	18	3	1

Table 3: Happel's model result of collector efficiency.

The results (Table 3) show some differences with respect to the literature curves of collector efficiency (eq. 3).

This can be explained by different reasons.

First of all we have also consider the electric double layer effect that it is not present in the eq. 3 formulation.

Moreover in eq. 3 the Brownian effect is consider as a diffusion coefficient, in our case we implement the mathematical formulation of a force, this could bring to different results.

Finally, more in general, the Lagrangian approach is different from an Eulerian approach.

The most critical point of our study it's the time step interval, the need of a very small time step interval in all our domain brings to very high computational efforts.

For this reason we are not able to release a lot numbers of particles and this is a limitation in our study.

Furthermore a smaller time step interval could perhaps lead to more precise results. But the software and the computer at our dispositions, in spite of its 32 Gb of RAM, couldn't allow us to use it.

In future works a better time discretization will be considered in order to have a better precision in our study. The possibility to use different criteria for particles motion (i.e. high time step in the bulk of the fluid, small time step close to the sand grains) would also be desired.

A further development would be to implement also particle-particle interactions.

4. Conclusions

Micro and nanoscale zerovalent iron is a promising reagent for the remediation of contaminated groundwater.

The aim of this study was to simulate, from a microscale point of view, the transport of iron nanoparticles, their interaction with the porous

media and their deposition on the porous matrix of the aquifer in order to calculate a collector efficiency and to derive an empirical formula useful for future field applications.

A Langrangian approach was used through the *Particle Tracing for fluid flow* module of COMSOL Multiphysics 4.2a.

This allowed us to calculate the particle trajectories in (i) a simplified domain, the Happel's model, and (ii) in a more realistic domain obtained from a SEM image.

The drag, Brownian, gravity, Van der Waals and electric double layer forces have been implemented.

Several limitations linked to the time step interval used from COMSOL to solve the model, did not allow us to calculate the complete trajectories of a lot numbers of particles.

For this reason we have no results from the simulations carried out in the realistic geometry, that obtained from a SEM image.

The Happel's model geometry was simpler and this allowed to conclude the simulations with a significance numbers of particles. The collector efficiency results show some difference from literature, this can be due to the choice of a Langrangian approach, to the implementation of the electric double layer force, not considered in other studies, and to the time step interval used.

Future developments of this work will include a better discretization and optimization of the model together with additional physical models such as the particle-particle interactions.

5. References

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6. Acknowledgements

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