



# A numerical model to simulate the NAPL source zone remediation by injecting zero-valent iron nanoparticles

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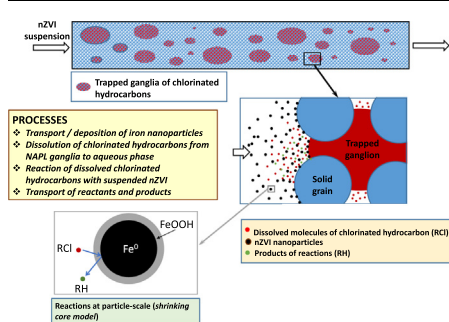
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## HIGHLIGHTS

- The fate of NPs is controlled by ripening/blocking (mech.1), and straining (mech.2).
- The reaction of nZVI with dissolved PCE is much faster than that with PCE ganglia.
- Particle sizes, nZVI reactivity, and solubility affect the NAPL remediation rate.
- The NPs aggregation is of high significance for the overall NAPL remediation rate.
- NAPL remediation rate is maximized as long as nZVI concentration is not depleted.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A continuum-scale numerical model is developed to simulate the flow, mass-transfer, and reactive processes taking place during the injection of zero-valent iron nanoparticles (nZVI) in a water-saturated porous medium, containing a chlorinated non-aqueous phase liquid (NAPL) at its residual saturation (source zone). Firstly, the transport of the nanoparticles (NP) is modelled by coupling the nanoparticles transport with their deposition in a porous medium. A systematic sensitivity analysis is done to examine the individual effect of each parameter on the spatial and temporal evolution of nanoparticle concentration along the column length. The parameters quantifying the kinetics of attachment/detachment between the nanoparticles and the porous medium (sand grains) are estimated via inverse modeling. Secondly, the kinetics of the reaction of nZVI with dissolved tetrachloroethylene (PCE) is based on the numerical predictions of the statistical shrinking-core model that couples the mass-transfer with the reactive processes taking place at a nanoparticle scale. The continuum NP transport model is then extended to include the reactive flows by combining the dynamics of PCE ganglia dissolution and nZVI reactions with mass balances for the residual PCE saturation, the dissolved PCE concentration, and the nZVI concentration in the aqueous phase. Sensitivity analyses are performed on the NP transport-NAPL remediation model with a view to clarify the effects of dimensionless parameters (dimensionless flow velocity, Damköhler numbers) on the fate of nZVI and trapped PCE ganglia. Finally, the residual PCE remediation efficiency is numerically predicted as a function of the injected NP mass. This efficiency is compared with the respective experimental results of a PCE source zone remediation test performed in a sand column, by using as adjustable parameters the kinetic coefficients of the nanoparticles deposition on sand grains. The remediation efficiency of the PCE source zone is maximized when the injected nZVI maintains its reactivity throughout its flow in the porous medium. To design an efficient NAPL source zone remediation strategy,

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the parameters must be set to values which will ensure that the nZVI is kept to a higher than zero concentration throughout the length of the porous medium.

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## 1. Introduction

In situ remediation of contaminated soils and aquifers has several advantages compared to the respective ex situ remediation techniques (Otten et al., 1997): (1) in situ remediation is more environmental friendly with regards to reducing volatile organic compounds (VOCs) emissions to the atmosphere, compared to the excavation, transport and ex situ treatment of the contaminated soil; (2) moreover, this method is applicable to sites that cannot be excavated (i.e. contamination under roads/constructions); (3) in most cases, the total cost of remediation is less using in situ methods in comparison to excavation and treatment; (4) when extracting contaminated groundwater and treating it above ground (ex situ pump-and-treat) by a variety of processes (e.g. air stripping, carbon adsorption, bio-reactors, chemical precipitation), highly contaminated wastes are produced and have to be disposed of in landfills.

However, the in situ treatment of contaminated aquifers has a number of inherent disadvantages (Pinder and Celia, 2006) including: (1) the difficulty of delivering agents to the contaminated zone (e.g. providing oxygen and nutrients for biodegradation processes); (2) the difficulty of determining the amount of treatment taking place; (3) the relatively low rates of treatment; (4) the potential to spread the contamination to new areas. With respect to the aforementioned issues, nanotechnology has a special relevance due to the combination of nanoparticles properties with fluid characteristics and thus the potential for injecting nano-sized (reactive or adsorptive) particles into contaminated porous media (e.g. soils, sediments, and aquifers). Among the various nano-materials explored for remediation, the nanoscale zero-valent iron (nZVI) is currently the most widely used for the in situ remediation of aquifers from a variety of toxic pollutants (e.g. reduction of chlorinated hydrocarbons, and nitro-aromatics, sorption/geochemical trapping of heavy metals/metalloids) (Mueller et al., 2012).

The mechanistic approaches commonly used to predict the colloid transport and deposition through porous media are based on the deep bed filtration mechanisms, such as interception, inertial impaction, sedimentation and Brownian diffusion and/or DLVO theory, which describes the colloid-collector interactions in terms of the adhesive and repulsive forces (Tien and Ramarao, 2007). From a continuum point of view, possible transport mechanisms of NP in porous media include reversible/irreversible deposition, agglomeration, straining, blocking, ripening, and size exclusion (Molnar et al., 2015; Babakhani et al., 2017).

The nZVI particles are engineered with surface coatings to inhibit aggregation (Phenrat et al., 2008), to decrease their adhesion to solid surfaces (Sirk et al., 2009; Saleh et al., 2008), and to reduce their reactivity (Phenrat et al., 2009a, 2010a). Nanoparticles can also acquire a natural coating once released into the environment due to the adsorption of natural organic matter (NOM) including humic and fulvic acids (Franchi and O'Melia, 2003). The proposed hypothesis for enhanced mobility is the electrosteric repulsions resulting from adsorbed charged macromolecules inhibiting attachment (Saleh et al., 2008). A coupled aggregation/colloid/transport model was developed to demonstrate how changes in particle size distribution can reduce the transport of carboxyl-methylcellulose (CMC) coated-nZVI in column experiments (Raychoudhury et al., 2012). The model was verified by comparing simulations with experimental and continuum modeling results

(Raychoudhury et al., 2012). A sensitivity analysis with another Lagrangian-type approach demonstrated the importance of time-dependent aggregation processes on nanoparticle mobility (Taghavy et al., 2015).

The continuum modeling of nanoparticle transport in porous media allows the estimation of kinetic parameters from lab-scale tests, as well as the rational design of field tests (Tosco and Sethi, 2010). A three dimensional, three phase, and finite difference numerical simulator was used to simulate nZVI and CMC transport in subsurface, and predict field-scale experiments under different injection scenarios (Chowdhury et al., 2015). To model the nZVI injection in the subsurface, the colloid flow and transport has been combined with multiphase mass-transfer and reactive processes by involving a great number of kinetic parameters (Tosco et al., 2009). Unavoidably, phenomenological models are used to describe the dynamics of transport phenomena (e.g. dissolution, volatilization, dispersion) and physicochemical interactions of nanoparticles with fluid (e.g. reactions) and solid (e.g. self-aggregation, grain deposition) phases (Lenhart and Saiers, 2003; Simunek et al., 2006; Grolimhd and Borkovec, 2006). Physicochemical and chemical processes have been shown to be strictly dependent on ionic strength and pH (Ryan and Elimelech, 1996) and hence the colloid transport equations must be coupled with mass balances simulating the transport of different ions in solutions (Lenhart and Saiers, 2003). Recently, Tosco and her collaborators (Tosco et al., 2009, 2014a, 2014b; Tosco and Sethi, 2010) have developed a multi-parameter continuum model of nano-colloid flow and transport in porous media and used it for interpreting lab-scale tests of increased complexity. It should be mentioned that the main drawback of such complex models is the increasing uncertainty of parameter values estimated by inverse modeling.

Straining is defined as the process in which particles get trapped in the throats of a porous network that are narrower than the size of the particles. In continuum-modeling, straining has been described either with a depth-dependent decaying exponential function (Bradford et al., 2003) or with a concentration-dependent decaying exponential function (Xu et al., 2008). The critical ratio of the particle diameter to the grain diameter for straining was found to be 0.0017 (Bradford et al., 2003; Li et al., 2004). However, this ratio cannot be valid for nanoparticles, mainly due to the interference of other mechanisms (e.g. aggregation, hetero-aggregation) (Toloni et al., 2014; Jones et al., 2014). Moreover, the hyper-exponential retained colloid mass profiles (RCPs) (decreasing rate of particles' deposition as the distance from the inlet grows) were attributed to straining (Bradford and Betahar, 2006; Wang et al., 2012). Hyper-exponential behavior of RCPs could also be attributed to other mechanisms, such as surface roughness, concurrent aggregation, particle population heterogeneity, porous medium heterogeneity, and variations in the flow velocity (Yuan and Shapiro, 2010; Babakhani et al., 2015). The depth-dependent model of Bradford et al. (2003) considers an attachment rate that decays with distance, which is favorable for predicting the behavior of the residual concentration profile, frequently observed in the transport of colloid and nanoparticles subjected to concurrent physicochemical filtration and straining (Tosco and Sethi, 2010). On the other hand, for studies in which a concentration-dependent model was used, the effect of physicochemical filtration had been turned off, and this brought about a nearly monotonic shaped RCPs (Babakhani et al., 2017).

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