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Review

Nanoscale zerovalent iron particles for groundwater remediation: a review

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ABSTRACT

Nanoscale zero-valent iron particles (nZVI) have been studied in recent years as a promising technology for the remediation of contaminated aquifers. Specific positive features of nZVI are the high reactivity towards a broad range of contaminants and the possibility of injecting in aqueous slurries for a targeted remediation of contaminated areas. However, crucial points to be addressed are stability against aggregation, mobility in subsurface environments, and longevity. In this work a review is presented on the current knowledge on the properties, reactivity and mobility in porous media of nZVI and their application to groundwater remediation. A specific focus is devoted to the methodologies to the colloidal stability of the nZVI slurries and to the available numerical tools for the simulation of laboratory and field scale mobility of the particles when injected in porous media.

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1. Zerovalent iron for groundwater remediation: from permeable reactive barriers to nanoscale particles

Permeable reactive barriers (PRBs) are a passive in-situ treatment of groundwater contaminated by organic and inorganic contaminants. PRBs are trenches excavated in the subsoil to intercept the contaminated plume, filled with a granular reactive material, eg. zerovalent iron (Gillham and O'Hannesin, 1994), activated carbon, zeolites, compost (Boni and Sbaffoni, 2009), etc, or with a combination of zerovalent iron with another material, eg. pumice (Moraci and Calabrò, 2010) or cotton (Rocca et al., 2007), which treats the contaminated groundwater passing through it under natural gradient. Granular zerovalent iron (ZVI) is the most commonly used filling material, thanks to its capability of degrading a wide range of organic contaminants, and reducing and immobilizing harmful metal ions (Orth and Gillham, 1995). To date, ZVI has been applied in the construction of hundreds of PRBs worldwide, in particular for the degradation of chlorinated solvents.

The main advantages of using PRBs include the almost immediate accessibility and availability of the site after the installation, the lack of external energy inputs, the limited requirements in terms of monitoring and maintenance (Zolla et al., 2007). Despite the (relatively) high installation costs, these aspects contribute to make PRBs a cost-effective remediation technology if compared to more traditional approaches, like Pump and Treat systems (Di Molfetta and Sethi, 2005). Over the past ten years, the use of PRBs has become an accepted standard practice for the treatment of a variety of groundwater contaminants (Di Molfetta and Sethi, 2012). Nevertheless, the emplacement and construction limitations restrain, in some cases, the applicability of this technology. Technical difficulties and high costs of excavation restrict the depth of the barrier to 30–40 m, hindering the treatment of deeper contaminations. Moreover, PRBs address their action to the contaminated plume, while direct treatment of the source of contamination is precluded. Besides, PRB long-term performance is a crucial point still under debate: the complex biogeochemical processes that occur inside PRBs can lead to mineral precipitation, gas accumulation and biomass growth, and progressively reduce the reactivity and permeability after the installation (Zolla et al., 2009). As a consequence, in some cases a regeneration of the barrier may be required, and several technical approaches have been proposed in this sense, including for eg. ultrasound systems for iron rejuvenation (Son and Vogan, 2004) or as a pre-treatment (Geiger et al., 2002), mechanical washing using high-pressure water jets

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(Gallo et al., 2004), and reduction of Fe(III) to Fe(II) mediated by iron-reducing bacteria (Shin et al., 2007).

In order to overcome some of these limitations, Wang and Zhang (Zhang et al., 1998) proposed the use of nanoscale zerovalent iron (nZVI) as an alternative to millimetric-sized particles. nZVI particles, thanks to their reduced size, much smaller than pores of aquifers, can be dispersed in aqueous slurries, and directly injected in the subsoil (Varadhi et al., 2005), thus allowing to directly target the contaminant close to the source of contamination (Tiraferri et al., 2008) (Fig. 1). Besides, the reduced size of nZVI results in a very high surface to volume ratio of nZVI particles (10–50 m^2/g) (Sun, 2006), three orders of magnitude higher than the ratio of granular iron (0.1–0.5 m^2/g), with a positive impact on degradation kinetics (Zhang, 2003). More recently, the use of larger particles, micrometric in size (microscale iron particles, mZVI) has also been proposed and investigated (Dalla Vecchia et al., 2009b). Both mZVI and nZVI were found effective in degrading most of the organic contaminants found in aquifer systems, and in particular chlorinated aliphatic hydrocarbons (Velimirovic et al., 2012a). nZVI exhibits, as a general rule, faster degradation kinetics (Almeelbi and Bezbaruah, 2012), but shorter lifetime compared to mZVI, due to high consumption via undesired reactions.

Several studies reported nZVI to be able to degrade a broad range of contaminants, even more than granular ZVI, thanks to the extremely high specific surface area, which makes reaction rates higher by orders of magnitude than those of millimetric iron (Lien and Zhang, 2001). However, the enhanced degradation rates of nZVI compared to granular iron (and, at a shorter extent, to mZVI) are not to be attributed to a “nano-effect”. Rather, degradation kinetics were observed to scale with specific surface area (O’Carroll et al., 2013) and to be influenced also by the presence of impurities and other metals (Yan et al., 2013).

The high reactivity of nZVI alone is not sufficient to ensure an effective remediation, and some important issues need to be addressed for successful full-scale applications. Crucial points are stability against aggregation, mobility in subsurface environments, and longevity under subsurface conditions (Tosco et al., 2012b). To be effective for in situ aquifer remediation, iron particles should remain in suspension for a time sufficient to allow slurry preparation, handling and injection in the subsurface. Also, they should have a sufficient mobility in the subsurface to be transported for some extent around the injection point (Kanel et al., 2007). However, several studies have shown nZVI to be scarcely mobile and stable in both laboratory studies (Liu et al., 2005a) and field-scale tests (Quinn et al., 2005). The main reason was found in the strong tendency of nZVI particles to aggregate when dispersed in water, due to the strong magnetic attractive forces which develop among particles, thus forming big dendritic flocs and subsequently network structures, which may widely exceed the micron. Such aggregates could also significantly limit transport by plugging the pores of the aquifer, and exhibit reduced specific surface area, and consequently reactivity (He and Zhao, 2005). A further limitation to nZVI mobility in the subsoil is also due to the eventual affinity between iron particles and minerals of the soil grains, thus resulting in nZVI deposition onto the porous matrix. Modification of particles surface and viscosity of dispersant fluid were shown effective approaches in improving both colloidal stability and mobility of nZVI.

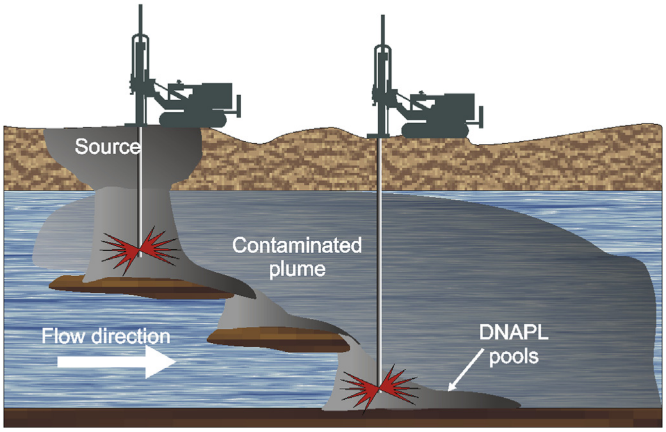

Fig. 1. Remediation of an aquifer contaminated by D-NAPLs injecting nZVI suspensions directly at the sources of contamination. Modified from Tosco et al. (2012b).

In this work a review of the current knowledge on nZVI properties, reactivity and mobility in porous media is provided. Particular attention is devoted to approaches for improving the colloidal stability and mobility of nZVI in porous media. For specific topics which have not been discussed into great details here, three recent reviews on the use of nZVI have been referred to, namely the works of O’Carroll et al. (2013); Yan et al. (2013); Crane and Scott (2012).

2. Synthesis and characterization of nZVI particles

Several techniques for the production of nZVI particles have been successfully applied in the recent years. They can be divided in bottom-up approaches (generation of iron nanoparticles from ions or smaller particles via nucleation, deposition, precipitation, agglomeration etc.) and top bottom approaches (size reduction of larger particles, eg. via milling, ablation, etc.) (Crane and Scott, 2012). The synthesis techniques reported in the literature usually follow the first approach, including decomposition of iron pentacarbonile [$Fe(CO)_5$] through standard chemical vapour condensation process in organic solvents (Karlsson et al., 2005), in argon (Choi et al., 2001) or in NH_3 (Kim et al., 2003), liquid precipitation of Fe^{3+} ions via reduction in presence of sodium borohydride ($NaBH_4$) (Wang and Zhang, 1997), and hydrogen reduction of goethite (FeOOH) and hematite (Fe_2O_3) (Nurmi et al., 2005). The latter process is applied for the synthesis of commercially available nZVI produced by Toda Kogyo Corp. The effect of ultrasound during synthesis in presence of sodium borohydride was recently considered with positive results in reducing the nZVI particles size and modifying their shape (Jamei et al., 2014).

In some cases, a further step in the synthesis process includes the deposition of a thin layer of another metal, which may be continuous or discontinuous, and is aimed at improving the iron reactivity as a catalyst (Chun et al., 2010), as well as modifying particles surface properties in order to improve colloidal stability (Hosseini et al., 2011). The secondary metals can be added in a second step via precipitation after synthesis of the iron particles, or via co-precipitation with hydrogen reduction of ferrihydrite or iron oxides in a solution of the secondary metal (Chun et al., 2010). The use of palladium, nickel and copper as secondary metals is reported in the literature (Yan et al., 2013).

The size distribution of nZVI primary particles obtained through the different methods is typically in the range of 10–100 nm, with a corresponding specific surface area in the order of 10–50 m^2/g (Sun, 2006). Nevertheless, dendritic aggregates, tens or hundreds of times larger than primary particles, are usually observed in aqueous dispersions of nZVI (Tiraferri et al., 2008), due to the strong particle–particle attractive interactions, as further discussed below (Fig. 2).

X-ray diffraction (XRD) analysis performed over a set of nZVI samples, both synthesized at laboratory and industrial scale (Liu et al., 2005b), revealed that particles are composed by a core of zerovalent iron and a shell of iron oxides and hydroxides, including

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