



# Agar agar-stabilized milled zerovalent iron particles for in situ groundwater remediation



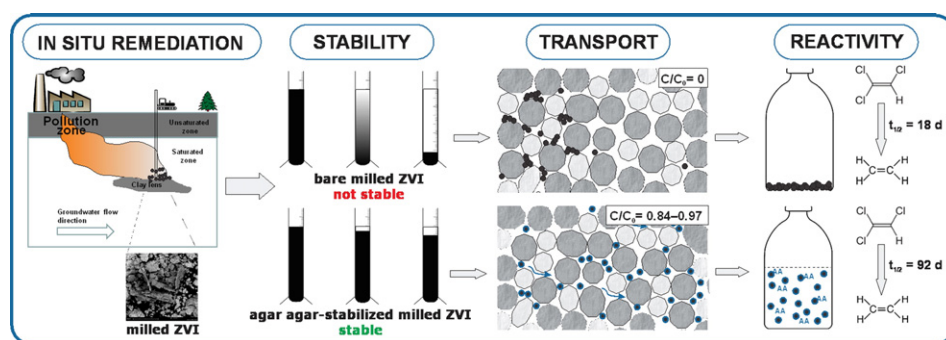
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## HIGHLIGHTS

- Rapid aggregation and sedimentation were observed in bare milled ZVI particles.
- Agar agar improved the stability of milled ZVI particle suspensions.
- Agar agar enhanced the transport of milled ZVI particles in heterogeneous sands.
- Agar agar reduced the reactivity of milled ZVI particles towards TCE.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Submicron-scale milled zerovalent iron (milled ZVI) particles produced by grinding macroscopic raw materials could provide a cost-effective alternative to nanoscale zerovalent iron (nZVI) particles for in situ degradation of chlorinated aliphatic hydrocarbons in groundwater. However, the aggregation and settling of bare milled ZVI particles from suspension presents a significant obstacle to their in situ application for groundwater remediation. In our investigations we reduced the rapid aggregation and settling rate of bare milled ZVI particles from suspension by stabilization with a “green” agar agar polymer. The transport potential of stabilized milled ZVI particle suspensions in a diverse array of natural heterogeneous porous media was evaluated in a series of well-controlled laboratory column experiments. The impact of agar agar on trichloroethene (TCE) removal by milled ZVI particles was assessed in laboratory-scale batch reactors. The use of agar agar significantly enhanced the transport of milled ZVI particles in all of the investigated porous media. Reactivity tests showed that the agar agar-stabilized milled ZVI particles were reactive towards TCE, but that their reactivity was an order of magnitude less than that of bare, non-stabilized milled ZVI particles. Our results suggest that milled ZVI particles could be used as an alternative to nZVI particles as their potential for emplacement into contaminated zone, their reactivity, and expected longevity are beneficial for in situ groundwater remediation.

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## 1. Introduction

The use of granular zerovalent iron (ZVI) in permeable reactive barriers (PRBs) is a well-established technique for in situ groundwater remediation of chlorinated aliphatic hydrocarbon (CAH) plumes through abiotic reductive dehalogenation (Gillham and O'Hannesin, 1992,

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1994; Lai et al., 2005; Matheson and Tratnyek, 1994). Although the in situ application of granular ZVI has been shown to be a promising alternative to conventional pump-and-treat techniques (Di Molfetta and Sethi, 2006; Gavaskar, 1999), this technique is invasive and is constrained by the installation limits (i.e. depth of the wall and accessibility). The innovative concept of an in situ reactive zone was introduced by Suthersan (1999) as an extension to the use of granular ZVIs in PRBs, and implemented by direct injection of fine ZVI particles (micron-scale and nano-scale; mZVI and nZVI, respectively), either under pressurized conditions or under gravity flow. This is in certain cases considered to be a more feasible and cost-effective technique than the use of PRBs (Li et al., 2006a; Luna et al., 2015; Velimirovic et al., 2014a). Moreover, mZVI and nZVI particles are far more effective at degrading a wide range of contaminants than granular ZVI, under laboratory conditions (Johnson et al., 1996; Scherer et al., 1998; Velimirovic et al., 2013; Zhang, 2003). However, widespread in situ application of nZVI and mZVI particles has not previously been possible due to (1) their rapidly decreasing surface reactivity as a result of corrosion processes, particularly for nZVI particles (Velimirovic et al., 2014b), (2) the limited transport distances for bare nZVI and mZVI particles, which is attributed to their rapid aggregation, agglomeration and sedimentation (Phenrat et al., 2007; Tiraferri and Sethi, 2009), and (3) pore clogging in the porous medium following particle injection (Cantrell et al., 1997; Kanel et al., 2007; Tosco and Sethi, 2010; Zhang et al., 2009).

Reduced aggregation and agglomeration of nZVI particles and a homogenous, stable particle suspension during injection have been to some extent achieved by modifying the particle surfaces by coating them with biodegradable and nontoxic polyelectrolytes and surfactants (Kanel et al., 2008; Phenrat et al., 2010; Raychoudhury et al., 2012; Schrick et al., 2004). Stable suspensions of both nZVI and mZVI particles can also be achieved by increasing their viscosity using shear-thinning solutions of biopolymers (Gastone et al., 2014; He et al., 2009; Tiraferri and Sethi, 2009; Tiraferri et al., 2008; Tosco et al., 2014; Xue and Sethi, 2012). A significant concern with the use of biopolymers for stabilization of nZVI and mZVI suspensions is the initial reduction in the reactivity of the particles. Particle reactivity can nevertheless recover after biopolymers become degraded and/or are rinsed off by groundwater (Imeson, 2009; Velimirovic et al., 2012). All aspects of nZVI and mZVI particles performance, including their suspension stability, mobility, and reactivity, therefore need to be understood, optimized, and critically evaluated when designing groundwater remediation (O'Carroll et al., 2013).

Many investigations have focused on the transport of stabilized nZVI and mZVI particles in artificial, mineralogically uniform porous media (Kim et al., 2009; Raychoudhury et al., 2012; Saleh et al., 2008). There have, however, been just a few investigations on the performance of these particles in natural, heterogeneous porous media from contaminated sites, which would be a prerequisite for designing field-scale applications. The few investigations that have tackled this issue (Basnet et al., 2015; Busch et al., 2014) have emphasized that the physical and geochemical heterogeneities in aquifers are likely to be critical to the transport of stabilized nZVI and mZVI particles. The mobility of stabilized nZVI and mZVI particles has already been shown to be affected by mineralogical diversity within an aquifer, and the associated heterogeneities in surface charge of mineral grains (Chen et al., 2001; Elimelech et al., 2000; Johnson et al., 1996; Kim et al., 2012; Laumann et al., 2013; Laumann et al., 2014; Yang et al., 2011). The texture of the sand within an aquifer has also been shown to influence the deposition and spatial distribution of stabilized nZVI particles that are retained within the aquifer (Phenrat et al., 2010; Raychoudhury et al., 2014). The impact of physical and surface charge heterogeneities encountered in natural sands deriving from contaminated sites in particular needs to be evaluated for the specific type of ZVI particles chosen for the remediation of these contaminated sites.

For our research we used an innovative type of submicron-scale zerovalent iron (hereafter referred to as milled ZVI particles) manufactured by milling mZVI particles (Köber et al., 2014), as an easy to handle and cost-effective alternative in comparison to commercially available nZVI particles (Li et al., 2006b). Preliminary investigations into the use of milled ZVI particles have shown that they offer a number of advantages over the extensively reported use of nZVI particles including relatively high reactivity towards CAHs, a longer lifetime, and low acute toxicity (Köber et al., 2014; Paar et al., 2015). Moreover, the newly designed milled ZVI particles are expected to be more reactive towards CAHs than recently introduced mZVI particles (Velimirovic et al., 2013). However, agglomeration (and even complete settling) of milled ZVI particles within suspensions (Köber et al., 2014) has proved to be an obstacle to efficient in situ application of these particles. One way to overcome this obstacle is through the use of high molecular weight polymers, which can improve the stability of a milled ZVI particle suspension (by increasing its viscosity), as previously proposed for nZVI and mZVI particles (Gastone et al., 2014; Tiraferri and Sethi, 2009; Tiraferri et al., 2008). Investigations into the stability of milled ZVI particles, their transport in different heterogeneous porous media, and their reactivity are therefore essential if efficient methods for in situ application of milled ZVI particles are to be designed that will improve their overall effectiveness for remediation of CAHs-contaminated groundwater.

The objectives of our investigations were therefore (1) to improve the stability of milled ZVI particle suspensions by selecting the most effective biopolymer stabilizer, (2) to evaluate the mobility of both bare and stabilized milled ZVI particles in different porous media including the ones from the contaminated sites, and (3) to investigate the impact of the selected stabilizer on the removal of CAHs by milled ZVI particles. A series of well-controlled column experiments were performed to investigate the influence of the grain size distribution, mineralogical and chemical variability of porous media on the transport of stabilized milled ZVI particles. A set of laboratory-scale batch reactivity experiments were also performed in order to determine the impact of the selected stabilizer on the reactivity of milled ZVI and to compare it with the reactivity of the bare material.

## 2. Materials and methods

### 2.1. Milled zerovalent iron particles

A batch of the newly developed milled ZVI particles in an aqueous suspension was supplied by UVR-FIA (Freiberg, Germany). The milled ZVI particles were manufactured in a two-stage process by (1) dry grinding iron powder (Atomet 57, Rio Tinto, Quebec Metal Powders Ltd), and (2) wet fine grinding using monoethylene glycol (MEG) as the grinding liquid, with the addition of a surfactant. The milled ZVI particles are described as irregular flakes a few micrometers across with a thickness of less than 100 nm and are polydisperse with a volume-based particle size ( $d_{50}$ ) of 11.8  $\mu\text{m}$  and zeta potential of  $-22 \pm 5$  mV (Fig. 1). The milled ZVI particles have a specific surface area of  $18 \text{ m}^2 \text{ g}^{-1}$  and an average  $\text{Fe}^0$  mass content of 85% (Köber et al., 2014).

### 2.2. Preparation of stabilized milled ZVI particles

The effect of five different high-molecular-weight biopolymers used in the food and pharmaceutical industries on the colloidal stability of the milled ZVI particles was first investigated (at a particle concentration of  $1 \text{ g L}^{-1}$ ). The tested biopolymers were agar agar (Setexam, Morocco), guar gum HV7000 (Rantec Corporation, USA), gum arabic (Argigum International, United Kingdom), carboxymethyl cellulose (CMC, Sigma Aldrich, Austria), and starch (Maizena, Unilever Austria GmbH, Austria). The properties of these stabilizers can be found in Supporting information (SI1). Milli-Q water (Millipore, Elix®5-Milli-Q® Gradient A10, SI2) solutions of the stabilizers were prepared with

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