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first published in:
Busch et al. (2011) Plating of nano zero-valent iron (nZVI) on activated carbon. A fast delivery method of iron for source remediation?. Geohydro 2011, Quebec, Canada. August 28-31 2011

Plating of nano zero-valent iron (nZVI) on activated carbon. A fast delivery method of iron for source remediation?*

Jan Busch[v], Tobias Meißner[‡], Annegret Potthoff[‡] & Sascha Oswald[v]

[v]Institute for Earth and Environment, University of Potsdam, Potsdam, Germany

[‡]Fraunhofer-Institute for Ceramic Technologies and Systems, Dresden, Germany

Corresponding author: J. Busch
jan.busch@uni-potsdam.de
+49 (0)331 9772649

Abstract

The use of nano zerovalent iron (nZVI) for environmental remediation is a promising new technique for in situ remediation. Due to its high surface area and high reactivity, nZVI is able to dechlorinate organic contaminants and render them harmless. Limited mobility, due to fast aggregation and sedimentation of nZVI, limits the capability for source and plume remediation. Carbo-Iron is a newly developed material consisting of activated carbon particles ($d_{50;3}$ = 0,8 µm) that are plated with nZVI particles. These particles combine the mobility of activated carbon and the reactivity of nZVI. This paper presents the first results of the transport experiments.

L'utilisation des nanoparticules de fer de valence zéro (nZVI) pour la dépollution est une nouvelle technique prometteuse pour la décontamination in situ. En raison de sa grande surface et sa grande réactivité, le nZVI est capable de déchloriner les contaminants organiques et de les transformer en substances inoffensives. L'agrégation et la sédimentation rapide des nZVI limitent la mobilité ainsi que l'aptitude pour la décontamination de la source et du panache. Carbo-Iron est un matériau nouvellement développé, composé de particules de charbon actif qui sont plaquées avec des particules de nZVI. Ces particules combinent la mobilité du charbon actif à la réactivité de nZVI. Cet article présente les premiers résultats des expériences de transport.

Der Einsatz von elementarem Nanoeisen ist eine vielversprechende Technik zur Sanierung von Altlastenschadensfällen. Aufgrund der hohen Oberfläche und hohen Reaktivität kann nZVI chlororganische Schadstoffe dechlorieren und zu harmlosen Substanzen umwandeln. Der Einsatz von Nanoeisen zur Quellen- und Fahnensanierung wird jedoch durch mangelnde Mo-

*This article was originally published in the proceeding of the Geohydro 2011 conference. Please cite this article as: Busch et al. (2011) Plating of nano zero-valent iron (nZVI) on activated carbon. A fast delivery method of iron for source remediation?. Geohydro 2011, Quebec, Canada. August 28-31 2011.

bilität im Boden im eingeschränkt. Carbo-Iron ist ein neu entwickeltes Material, das auch Aktivkohlepartikeln ($d_{50;3}$ = 0,8 µm) und nZVI besteht. Diese Partikel kombinieren die Mobilität von Aktivkohle mit der Reaktivität von nZVI. Dieser Artikel beschreibt erste Ergebnisse von Transportuntersuchungen.

1 Introduction

Clean water is considered to be one of the most important resources for human and environmental health. Therefore soil and groundwater contamination is one of the biggest threads to a clean environment. Organic and inorganic contaminants, such as chlorinated hydrocarbons and metallic ions, represent a wide range of pollution which has been subject to remediation for several decades. One new approach for environmental remediation is the use of Nanotechnology, which is considered to be a beneficial technology for the sustainable management of groundwater resources (Grieger et al., 2010). Therefore, several applications for the use of nanotechnology are currently under investigation. These are decontamination of air, nanofiltration for water purification and soil and groundwater remediation by nanoparticles, (Mueller and Nowack, 2010). Functional nano-materials can be separated into four classes (1) metal-containing nanoparticles, (2) carbonaceous nanomaterials, (3) zeolites, and (4) dendrimers. All classes have different physicochemical properties and are therefore used in different applications (Savage and Diallo, 2005).

The first group, metal-containing nanoparticles, is promising for soil and groundwater remediation and could be applied parallel to or instead of common technologies, such as pump- and treat technologies or installed permeable reactive barriers. General introductions to nanoparticles (Nowack and Bucheli, 2007) and the use of nanotechnology in environmental remediation (Savage and Diallo, 2005; Mueller and Nowack, 2010) is also available as introductions dealing with nanoscale zero-valent iron (nZVI) (Zhang, 2003; Lowry, 2007), which will be focused on here. Organic pollutants can be dechlorinated by zero-valent iron (ZVI) according to the following equation:

$$\text{R-X} + Fe^0 + H_2O \rightarrow \text{R-H} + Fe_2 + OH^- + Cl^-$$

Using this mechanism, Trichloroethylene (TCE), for example, can be reduced by ZVI to acetylene (Lowry, 2007), and therefore be rendered to a less harmful substance. In this process the ZVI does not act as a catalyst, but is consumed. The use of Milimetric ZVI in PRBs is an approved technology for plume remediation and has been applied for many years (Matheson and Tratnyek, 1994). By using nZVI instead of granular ZVI, nanosize-effects change the properties of the material. Due to the high surface area, the reactivity of nZVI is several orders of magnitude higher than the reactivity of granular ZVI (Mueller and Nowack, 2010). Another advantage of using nZVI could be the easier application compared to permeable reactive barriers (PRBs), since a cost intensive installation could be exchanged with direct injection of nZVI-containing slurry. However, a review of different approaches for application of ZVI, from nano to milimetric scale using different inplementations shows high cleaning efficiency for all ZVI applications, but concludes a need for research exists on nZVI applications for source and plume remediation to reach cleaning efficiencies as high as the efficiency of PRBs (Comba et al., 2011).

Fast aggregation of nZVI in soils was identified to be the main limitation for application (Phenrat et al., 2007), which leads to short transport distances in soils (Schrick et al., 2004) and therefore direct injection might not lead to closed PRBs which prune the plume of a contamination completely. Several approaches have been made to enhance the mobility of nZVI in soils: On the one hand there are approaches using a polymeric surface modifier, such as guar gum (Tiraferri and Sethi, 2009), carboxymethyl cellulouse (CMC) (He et al., 2010), or other modifiers (Phenrat et al., 2008; Kim et al., 2009). On the other hand there are approaches using mobile particles as carrier, such as silica (Zhan et al., 2008; Zheng et al., 2008) or carbon particles (Mackenzie et al., 2008; Sunkara et al., 2010).

Newer approaches aim for a carrying particle which can be transported in soils further than stabilized nZVI particles. According to filter theory, particles having a size of 1 µm show the highest mobility in soils (Tufenkji and Elimelech, 2004). Therefore composite materials are a promising approach for the fast delivery of nZVI. Carbo-Iron particles are nZVI and carbon-containing composite materials. These particles were initially described by Mackenzie, et al. (2008) and are under development from lab scale to large scale production. The new approach uses activated carbon colloids, in a solution of iron(III)-ions, which is dried and the iron is reduced to Fe0 thermally by hydrogen (Bleyl et al., 2011; Mackenzie et al., submitted). This study aims to provide first information on material characteristics and transport characteristics of Carbo-Iron particles.

2 Materials and Methods

2.1 Particle characterization

Carbo-Iron particles were provided by the Helmholtz-Centre for Environmental Research – UFZ, Leipzig, Germany. For this initial investigation, the aim was to work with inert (unchanging) particles. Therefore the powder was stored six weeks in tap water to yield deactivated nZVI. The particle size distribution of suspended Carbo-Iron was measured by means of static light scattering using a Mastersizer 2000 (Malvern GmbH, Herrenberg, Germany). Therefore, suspensions were obtained by probe sonication taking a Branson Sonifier 450 (Branson Ultrasonics Corporation, Danbury, CT, USA). Specific surface area (BET method) was obtained by taking an ASAP 2010 accelerated surface area and porosimetry analyzer (Micromeritics GmbH, Mönchengladbach, Germany). Scanning electron microscopy (SEM) images were taken from the powder using a Zeiss ULTRA 55 (Carl Zeiss SMT, Oberkochen, Germany).

The dispersant carboxymethylcellulose (CMC) was purchased under the trade name Antisol FL 30 from Wolff Cellulosics (Walsrode, Germany). Suspensions were prepared with different amounts of CMC and their zeta potential was measured by using a Zetasizer Nano (Malvern GmbH, Herrenberg, Germany).

2.2 Column tests

Commercially available sand was used from Euroquarz GmbH (Laußnitz, Germany) in the sizes of 0.001-0.25 mm, 0.1-0.5 mm, 0.2-1.0 mm and 1.0-2.0 mm grain size. Breakthrough tests were performed using constant flow conditions of 2.5 mL/min using a peristaltic pump coupled to chromatography columns with a diameter of 3 cm and a length of 60 cm (Carl Roth GmbH, Karlsruhe, Germany). The flow direction was vertically against gravity. The columns were filled wet, yielding a porosity of 0.38-0.39. Porosity was measured gravimetrically. Filled columns were cleaned and equilibrated with deionised water until the electrical conductivity at the outflow was less than 1 µS/cm (>10 pore volumes (PV) exchange).

Samples were prepared by adding 100 mg Carbo-Iron into 1 L deionised water and sonication for 1 h. Afterwards the samples were stabilized by adding CMC in various concentrations (in % related to the amount of Carbo-Iron) and the sample was sonicated for another 1h. Samples were used directly after production. Measurement of the particle concentration was performed using an electrical conductivity meter at the end of the column. The measured conductivity was logged every 15 minutes.

3 Results and discussion

3.1 Particle characterization

Carbo-Iron powder consists of nearly spherical agglomerates with diameters up to several sizes of 10 micron as shown in Figure 1. Further, high porosity within the agglomerates is clearly visible. The measured specific surface area was 682 m^2/g which thus reflects the obvious porosity of Carbo-Iron in the SEM image.

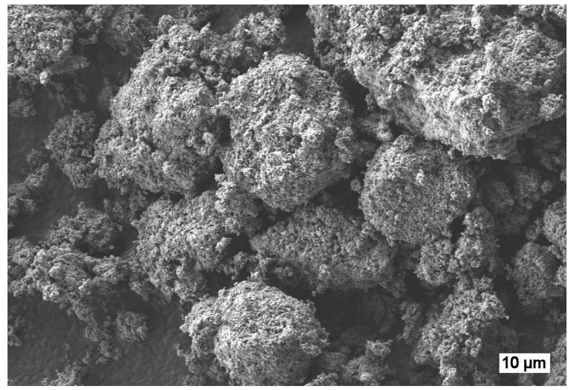

Figure 1: SEM image of Carbo-Iron

In suspension and after sonication treatment, a $d_{50;3}$ of 0.84 µm was obtained, meaning a significant reduction of the particle size of Carbo-Iron in comparison to the raw powder. Thus, the sonication process effectively destroyed the existing agglomerates.

After dispersing Carbo-Iron, a zeta potential of approximately 10 mV was observed. This value is too low for an electrostatic stabilization of the Carbo-Iron particles. Therefore, different amounts of the biocompatible polymer CMC were tested to get a stable suspension.

The addition of CMC resulted in a zeta potential switch from formerly positive values to negatives ones. Furthermore, with increasing mass percentage of CMC, the zeta potentials become smaller, i. e. more negative which means an increase of electrostatic repulsion forces. The charge reversal also gives proof of an adsorption of CMC onto the Carbo-Iron surface.

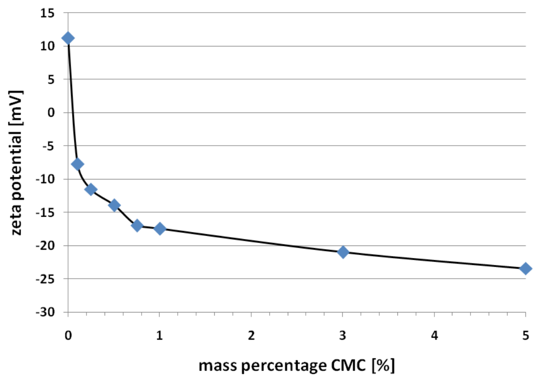

Figure 2: Zeta potential of Carbo-Iron suspension containing different amounts of CMC.

3.2 Column tests

Electrical conductivity could be applied as the detection method for the concentrations of CMC-stabilized and unstabilized Carbo-Iron suspension in deionised water with a linear coefficient of R^2=0.99 in the required range (Figure 3).

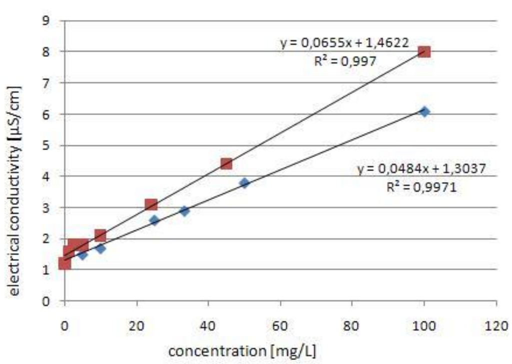

Figure 3: Electrical conductivity of different concentrations of CMC-stabilized (red square) and unstabilized (blue diamonds) Carbo-Iron containing suspensions.

Results show breakthrough in three of four tested sands. Particles could not pass the finest sand with a particle size of 0.001-0.25 mm in this experiment. The particles did not pass the first millimetre of the porous medium and after a short time the column was blocked. The blocking might rather be related to aquitard characteristics of the porous media than to the addition of Carbo-Iron particles. Breakthrough of Carbo-Iron particles with 5% CMC in the other columns was observed to begin shortly after the first exchanged pore volume and reached a plateau within the first three exchanged PV. In this experiment the ratio of input and the output concentration reached between 0.5 and 0.8 (Figure 4).

Breakthrough using different amounts of CMC showed no breakthrough for CMC concentrations of 0.0% and 0.25% without any blocking of the column. The plateau of breakthrough for 0.5% CMC was reached after ten PV and for 5.0% CMC at three PV. The more efficient transport of Carbo-Iron with increasing amounts of CMC can be attributed to the better electrostatic repulsion of the particles, indicated by the reduced zeta potential.

Comparable breakthrough times have been observed for nZVI containing silica composites in column tests before (Zhan, et al., 2008), therefore this product is comparable to other particle based supported nZVI products. Compared to pure and stabilized nZVI, the breakthrough in the columns is significantly faster (Schrick, et al., 2004), which is one of the most important aims in developing these particles. Incomplete breakthrough has been observed before for different particles in comparable ranges (Lecoanet et al., 2004). The mechanism for filtration and attach-

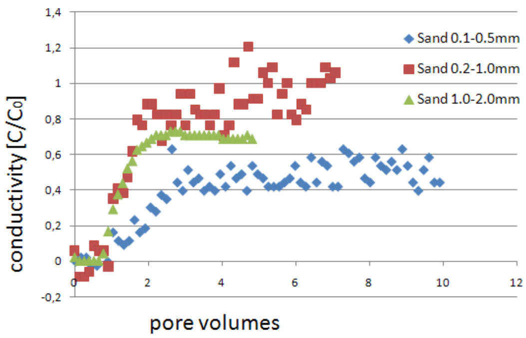

Figure 4: Breakthrough curves of Carbo-Iron particles in porous media of different grain sizes. The porous media consist of sand with grain sizes of 0.1-0.5 mm, 0.2-1.0 mm and 1.0-2.0 mm. Carbo-Iron particles were stabilized using 5% CMC.

ment seems to be related to the size of the porous media. According to filtration theory, particles start getting filtrated by the porous medium if the particles are larger than 0.05% of the particles of the porous media (McDowell-Boyer et al., 1986), which might explain the filtering in the sand with grain sizes of 0.001-0.25 mm. Nevertheless, this material seems to have aquitard characteristics and therefore might be irrelevant for remediation. In fine sand with grain sizes of 0.1-0.5 mm, the transport characteristics seem to be related to the content of stabilizer in the suspension. While Carbo-Iron suspensions with less than 0.25% of CMC are not mobile, higher contents of CMC make Carbo-Iron mobile. This is explainable by the zeta-potential of the particles which changes from positive to negative with addition of CMC. However, the absolute value of the zeta potential rises with addition of CMC. Therefore transport using 5% CMC is faster than using 0.5% CMC. In general, organic material is known to enhance transport of particles in soil (Aiken et al., 2011), which might open the possibility to use different kinds of organic stabilizers depending on the needed application or underlying regulation. However, agglomeration and fractioning of the particles during transport will be investigated later.

This method of detection is usable only in deionised water without addition of any conductivity changing agents such as salts, acids or dissolved organic material. Additionally, full coating of the surface by CMC is reached at 7% (unpublished data); here only 5% was used, because unattached stabilizer could have an effect on the measurement. Therefore factors affecting the transport properties of Carbo-Iron need to be investigated by a different method prior to a field test, which is planned for the end of 2011. A promising technology for investigating on transport of these particles is the analysis of carbon content, as used before (Mackenzie, et al., 2008). Further investigations will focus on changing transport properties at different pH and ion concentrations by detection of carbon or iron content of the suspension.

4 Conclusions

Carbo-Iron is a newly developed composite material containing nZVI, which is immobilised on activated carbon. The aim in developing this material is to provide a highly mobile material for groundwater remediation in soils. This study showed potentially high mobility in soils, which was showed by column tests. Compared to pure and stabilized nZVI, the transport is faster and therefore higher transport ranges can be expected. Future work will focus on improving the characteristics of Carbo-Iron and optimization of the delivery procedure to develop an efficient application for groundwater remediation.

Acknowledgements

This study was supported by the German Ministry for Education and Research (Bundesministerium für Bildung und Forschung, BMBF) in the project Fe-NANOSIT (Iron based nanoparticles and nano-composite structures for remediation of ground- and wastewater). We want to thank the Environment Research Centre Leipzig (UFZ, Leipzig, Germany) for provision of the Carbo-Iron particles.

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