

COLLOIDAL ACTIVATED CARBON AND CARBO-IRON – NOVEL MATERIALS FOR *IN-SITU* GROUNDWATER TREATMENT

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ABSTRACT

Two novel materials have been developed and tested in initial studies for the *in-situ* generation of sorption and reactive barriers for subsurface water treatment at low cost by introducing sorbents or reagents via injection wells. Both materials are based on finely-ground activated carbon with a particle size of $D_{50} = 0.8 \mu\text{m}$ which is quasi-soluble, i.e. it forms stable colloidal solutions in water over a wide concentration range. With these activated carbon colloids, an approved material of environmental technology is now applicable for injection into contaminated aquifers to form sorption barriers by controlled deposition on aquifer sediment directly in the flow passages. A new remediation strategy can be followed – the *in-situ* generation of a permeable AC sorption barrier in contaminated aquifers.

Based on the colloidal carbon particles, a second material has been developed which combines the sorption properties of the activated carbon carrier and the reactivity of the zero-valent iron deposits. This CARBO-IRON (20 wt-% zero-valent iron) has proved its suitability as a dehalogenation reagent applicable for both plume and source treatment.

KEYWORDS: Zero-valent iron, activated carbon, CARBO-IRON, dechlorination, sorption-assisted reaction, particle transport, groundwater treatment, plume and source treatment

1. INTRODUCTION

Groundwater treatment using permeable reactive barriers (PRBs) is a promising remediation strategy for a variety of inorganic and organic pollutants. Approved chemical and physical methods are applied, sometimes in combination with biotic degradation processes (Simon and Meggyes, 2000). During the last decade, intensive research has been carried out on the development of suitable materials for reactive barriers in subsurface application. The most extensively studied and applied PRB type uses granular iron particles (Korte, 2001). Zero-valent iron (ZVI) acts as reducing agent and is oxidized to ferrous iron. Iron-bearing PRBs are mainly applied for the degradation of halogenated hydrocarbons (R-X) (Gillham and O'Hannessian, 1994). The pollutants are removed from the groundwater as follows from the equation: $\text{R-X} + \text{Fe}^0 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{R-H} + \text{OH}^- + \text{Cl}^-$.

Another often-followed remediation strategy is the sorptive extraction of hydrophobic pollutants from contaminated waters into sorption-active phases. In aquifers, organic hydrophobic contaminants are retarded by any natural material with high organic carbon content (Cohen, 1991). Even more efficient is the adsorption onto activated carbon (AC) which is already used for ex-situ cleaning of drinking water (Jekel, 1979). In PRB approaches of the sorption type for groundwater treatment, granular AC is used mainly in funnel & gate constructions. Sorptive removal can be a good solution for the attenuation of highly or at least moderately hydrophobic organic compounds ($\log K_{\text{OW}} > 3$) (Simon and Meggyes, 2000). For these pollutants the values of K_d on AC (between 10^3 and 10^7 l kg^{-1} for BTEX and PAHs) are high enough for a sufficiently long retardation under equilibrium conditions (Gratwohl, 1997; Schad and Gratwohl, 1998) which ensures lifetimes in the orders of years.

Iron walls have already been constructed at more than 120 sites worldwide and count as an approved technology (Simon, 2006). Compared with conventional metal particles nano-sized metal particles have some advantages: their high specific surface area allows higher reaction rates, which can be 10 to 1,000 times higher for nano-sized ZVI (nZVI) than those found for granular ZVI (Wang and Zhang, 1997). Recently, the application of nano-sized particles has been advanced, because colloidal solutions of metal particles can easily be injected into the aquifer without the necessity of extensive underground work. This fact and the potential of nZVI to migrate in groundwater to form a reactive zone have stimulated the research on nanoparticles (Zhang and Elliot, 2006). A technology was born for truly *in situ* generating of PRBs.

However, pure nZVI is not sufficiently mobile under aquifer conditions and is not well suited for source remediation (Schrack *et al.*, 2004). The iron surface charge needs to be altered in order to avoid agglomeration and untimely sedimentation. Addition of emulsifiers to a suspension of nZVI forms emulsion droplets which contain the ZVI particles in water surrounded by an oil-liquid membrane. Emulsified zero valent iron (EZVI) has been tested in a field-scale demonstration (Quinn *et al.*, 2005). The material was injected into the saturated zone in order to enhance *in situ* dechlorination of dense, non-aqueous phase liquids (DNAPLs). EZVI proved miscible with the organic phase; therefore, contact between the reaction partners was realized leading to subsequent dechlorination. Nevertheless, the addition of chemicals to the reactive agent is necessary in order to achieve the close contact between the reactants and the resulting emulsion is relatively viscous.

The objective of our work is to develop materials with tailored properties for *in-situ* generation of sorption and reactive barriers for subsurface water treatment at low cost and without the need for additional chemical supply. Based on the known methods in abiotic water treatment by means of PRBs (sorptive pollutant elimination and pollutant destruction by chemical reaction) this study focused on AC as sorbent and ZVI as reactant. Both materials should be provided in such a form that stable colloidal solutions can be introduced into the saturated zone via injection wells. Moreover, the developed material is a promising candidate for direct source removal in case of residual DNAPLs.

2. EXPERIMENTAL

Chemicals. Ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) p.a., ferrous chloride (FeCl_2), calcium chloride (CaCl_2), dichloroethene (DCE) and 1,1,2,2-tetrachloroethane (TeCA) were purchased from Merck KGaA (Germany). Trichloroethene (TCE) and tetrachloromethane (Tetra) were purchased from Sigma-Aldrich (Germany) and NaBH_4 obtained from Hilde GmbH (Germany). All chemicals were used without further purification. As reference a slurry with reactive nano iron particles (RNIP) was purchased from Toda Kogyo Corp. (Japan, found: 50 wt% Fe^0 ; nominal: 60 wt% Fe^0 ; BET surface area $38 \text{ m}^2 \text{ g}^{-1}$ based on information of Toda/Kogyo). Humic acid (Roth-HA) was obtained from Carl Roth GmbH (Germany).

Activated carbon. The AC Hydriffin PR was purchased from Donau Carbon GmbH (Frankfurt/M., Germany, $D_{75} = 40 \mu\text{m}$; point of zero charge (PZC): 8.8) and used as received. The AC SA Super was purchased from Norit Deutschland GmbH (Duesseldorf, Germany) and ground in the presence of deionized water using a horizontal mill 200 AHM (Hosokawa Alpine AG, Augsburg, Germany). By means of laser diffraction measurements, a particle size distribution characterized by $D_{50} = 0.8 \mu\text{m}$ and $D_{90} = 1.6 \mu\text{m}$ (Metasizer, Malvern Instruments Ltd., UK) was determined. The PZC was found at $\text{pH} = 8.2 \dots 9.0$ (potentiometric titration and immersion technique).

Preparation of nano-ZVI. The particles were synthesized by reduction of an aqueous solution of FeCl_2 by NaBH_4 using a slightly modified method previously described in (Liu *et al.*, 2005). By means of REM measurements the average particle size was found to be $16 \pm 2 \text{ nm}$. Accordingly, the specific surface area was calculated to $40 - 50 \text{ m}^2 \text{ g}^{-1}$. The ZVI content was 40 wt-% (measured as H_2 evolution during total particle dissolution in aqueous HCl).

Dehalogenation batch experiments. The dehalogenation studies were carried out as batch experiments. 250-mL amber screw-cap bottles equipped with Mininert[®] valves were used. Between 20 mg and 1.4 g Fe^0 were added to 200 ml reaction solution (typically deionized water, tap water, 0.1 M $\text{NH}_3/\text{NaNH}_4$ buffer solution or 50 mg l^{-1} solution of polyanionic

stabilizer) which was extensively purged with N₂ prior to adding the nano-ZVI or CARBO-IRON. After additional N₂ purging and re-dispersion for a few minutes in an ultrasonic bath, the desired amount of HOC as methanolic solution was added (reaction start). From this point on, the bottle was continuously shaken (60 rpm) throughout the experiment. The reaction kinetics was monitored by means of headspace analyses of dehalogenated products using a GC-MS device (QP 5000, Shimadzu Corp., equipped with a DB1 thick film capillary column). In addition, the reaction product halogenide was analyzed using an ion chromatograph (IC25, Dionex, equipped with an IonPac[®] AS15/AG15 column set).

Preparation of CARBO-IRON. 500 g AC and 1080 g Fe(NO₃)₃·9H₂O (= 150 g Fe³⁺) were mixed in 1L of water and shaken overnight. The water was removed using a rotary evaporator. The re-ground residue was transferred into a quartz glass reactor and heated up to 350°C under nitrogen atmosphere (50 ml min⁻¹) to complete the cleavage of nitrate and the dehydration. Afterwards, the iron oxide/AC system was reduced with hydrogen (50 ml min⁻¹) in the temperature range 500 to 600°C for 48 h and allowed to cool down under nitrogen atmosphere. All manipulations concerning the fresh CARBO-IRON were performed under nitrogen according to standard Schlenk techniques. Before handling as a dehalogenation agent, the fresh CARBO-IRON was subjected to a specially adjusted deactivation step. In water, CARBO-IRON can easily be extracted from unwanted by-products by magneto-separation.

TEM analyses. The transmission electron microscopy (TEM) measurements of the Fe⁰/AC-particles were made as followed: the carbon powder was embedded into a resin (M-Bond 610) to form a bulk sample. This was prepared by means of mechanical grinding, polishing and finally by Ar⁺ ion thinning. Typical operation conditions employed are an accelerating voltage of 4 kV, a beam current of 0.5 mA and a beam incidence angle of 11...13°. TEM and TEM-EDX examinations were carried out using a Philips CM 200 STEM equipped with a super twin objective lens (point resolution 0.23 nm). The average chemical composition of the iron particles was determined by EDX-analysis. To measure the particular compositions of the small Fe-containing particles, the spot diameter was reduced to about 5...10 nm (nanoprobe mode). In order to obtain reliable quantitative results the EDX-system was calibrated by determining the Cliff-Lorimer factors k_{AB} using standard samples.

Column experiments and mobility studies. The column experiments were carried out using a glass column ($d_i = 2.6$ cm, $l = 75$ cm) packed with a sieved fraction (0.25...1 mm) of original aquifer material (Zeititz megasite, Germany). The columns were packed to an average porosity of 30 % and placed in a vertical orientation. In all of the experiments the pH of the mobile phase was equal to the pH of the AC suspension. A syringe pump injected the colloid suspension (100 mg l⁻¹ AC in water) into the mobile phase before it flowed through the column. Various aqueous solutions with different ionic strengths were used as the mobile phase, pumped through the column by a plunger pump smoothed flow. The total flow used in the experiments was 4 ml min⁻¹ corresponding to a Darcy flow velocity of 2.8 cm min⁻¹. During and after the injection of the AC suspensions, the effluent was cut into samples of 2...10 ml and the carbon content of these samples was determined by a Total Carbon Analyzer.

3. RESULTS AND DISCUSSION

This paper deals with two alternative approaches for providing injectable material for groundwater treatment, which are both based on finely-ground AC. Both materials were considered as basis for a new composite material to be provided in such a form that stable colloidal solutions can be introduced into aquifers via injection wells. A key property of *in-situ* reagents is their mobility within the aquifer. By adjusting to an optimum mobility the number of injections necessary for constructing a continuous treatment zone can be reduced. From the colloid filtration theory it is known that natural aquifer particles in the lower micrometer-scale are more mobile than those in the nanometer-scale. The characteristic curve of the so-called 'single-collector-efficiency' over the particle size has a minimum at around one micrometer for low-density particles (Tufenkji and Elimelech, 2004), which is the same size range we chose for the colloidal AC particles. Laboratory and scale-up studies were carried out in order to

investigate mobility and deposition characteristics of colloidal AC flushed into fixed beds of original aquifer material both with and without natural and synthetic polyanionic stabilizers.

As expected, the experimental results showed that the non-stabilized colloids become less mobile with increasing ionic strength. In the presence of cations the electrostatic repulsion between the negatively charged surfaces of the mineral grains and the colloids is lower. The increase in the ionic strength of the solution also diminishes the electrostatic repulsion between the carbon colloids themselves, so that their agglomeration is favoured. A long-term objective of our work is the control of the transport behaviour of AC colloids in the aquifer by selective variation of the ionic strength of the eluent water: the construction of the barrier in the aquifer could be performed by injection of a suspension of colloidal AC in deionised water, where the colloids are transported by the groundwater flow. Due to certain dissolution of aquifer material and spontaneous mixing with the saline groundwater in the border zones, the AC colloids would be immobilised on the aquifer sediment, resulting in an aquifer zone enriched with activated carbon in the preferred groundwater flow passages – an effective sorption barrier. The sorption capacity of such a barrier can be increased by means of further injections of AC and can therefore be adapted e.g. to changes in the contaminant concentration of the groundwater or to prolonged periods of use.

However, AC can only create a sorption barrier. The second aim of our research is to expand the idea of the *in situ* flushed-in sorption barrier in the direction of a reactive sorption barrier. We gave the colloidal carbon material additionally the reactivity of ZVI by impregnating the AC particles with iron salts followed by reduction at elevated temperatures with hydrogen. The procedure results in activated carbon with iron nano-clusters. We call this new composite material CARBO-IRON. With this reagent a new remediation strategy can be followed – the *in-situ* generation of a permeable sorption/reaction barrier in contaminated aquifers.

Compared to pure nano-iron which is neither sufficiently mobile nor well-suited for source remediation, it was found that the novel composite material CARBO-IRON showed advantages for both purposes. Figure 1 shows that both components, AC and ZVI, are in close contact. Iron forms predominantly clusters in the size range of 20...50 nm. However, larger crystallites (> 100 nm) can also be found. The TEM bright-field image and the selected area diffraction pattern (SAD) measurements of the Fe particles prove the crystallinity of the ZVI clusters. With the iron-modified AC the full sorption activity of the sorbent was preserved. Our concern was that the close contact of AC and ZVI does not automatically mean that hydrophobic substances which are sorbed to the AC carrier are easily available for reduction at the Fe centres.

However, CARBO-IRON (15...20 wt-% ZVI) proved its dehalogenation activity for chlorinated and brominated C₁ and C₂ hydrocarbons in aqueous solution. The dehalogenation experiments using carbon tetrachloride, trichloroethene, 1,1,1,2-tetrachloroethane, 1,2-dibromoethene and vinyl bromide confirmed CARBO-IRON's high dehalogenation potential. The pollutants are collected and enriched at the AC surface. The basic prerequisite for a successful destruction of the pollutants is their availability at the Fe clusters for reductive dechlorination. CARBO-IRON showed similar activities in batch and column tests, indicating accumulation and successive supply of pollutant by the carrier. Lifetimes of the material in the order of several weeks have already been achieved in laboratory studies.

Nano-sized ZVI can be produced by reduction of iron precursors using NaBH₄ in aqueous solution (Fe^B) or using H₂ in the gas phase at elevated temperatures (RNIP). The differences between these two types of nano-particles concerning structural properties and reactivity for the dehalogenation of HOCs have been intensively studied (Nurmi *et al.*, 2005). The chemical nature of the ZVI surface was found to be very important for the reduction reactivity (boron-doped surface versus magnetite shells). Magnetite shells are believed to hinder the electron transfer from the iron to the HOC (Liu *et al.*, 2005).

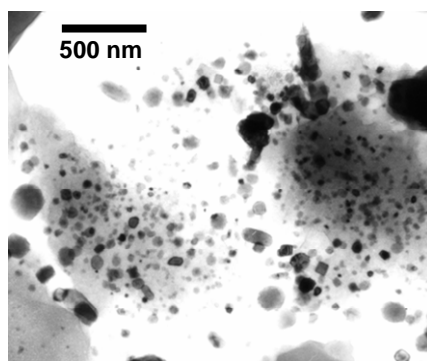


Figure 1. TEM bright-field image of iron particles on carbon grains (CARBO-IRON) with 20 wt-% zero-valent iron

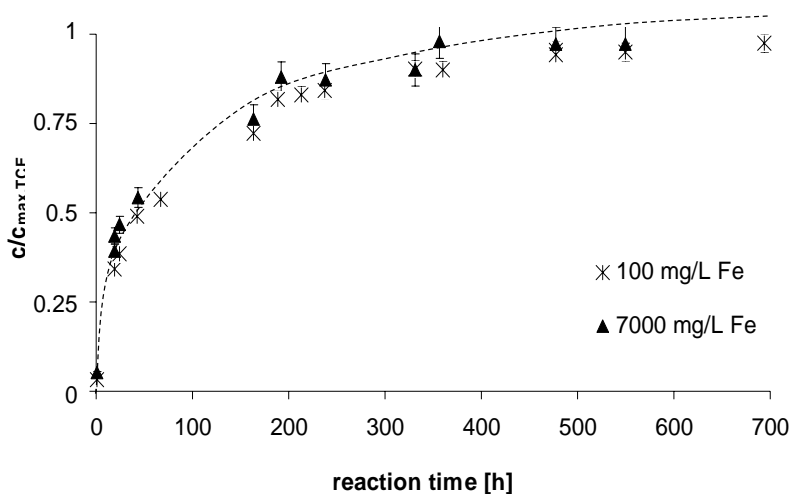


Figure 2. Observed reaction kinetics for the dechlorination of TCE to ethene/ethane using various concentrations of CARBO-IRON. ($c_{0,TCE} = 0.23$ mM, 0.1 M NH_3/NH_4^+ buffer, yields: $c/c_{max,chloride} = 100\%$, $c_{max,C2}$ hydrocarbons = 40...45% of $c_{0,TCE}$)

The synthesis of CARBO-IRON is similar to that of RNIP with hydrogen as reducing agent. Therefore, particular attention was paid to a mild deactivation step avoiding the formation of a retarding magnetite shell around the Fe nano-clusters. According to our experience this deactivation step is crucial for the reactivity and longevity of the ZVI.

In the batch experiments all of the HOCs mentioned above were reduced using pure nano-ZVI as described by other working groups. The observed reaction rate with $7 \text{ g l}^{-1} \text{ Fe}^0$ was in the same order of magnitude as known from the suspensions of commercial nano-iron with the same Fe^0 concentration. However, the reductive dehalogenation takes place with a similar reaction rate apparently independent of the CARBO-IRON concentration. Figure 2 shows that widely varying CARBO-IRON concentrations seem to have no drastic effect on the observed reaction rate. This effect can be interpreted with the help of equations (1) to (4). Eqs. (1) and (2) are valid for ZVI and eqs. (3) and (4) for CARBO-IRON. They show that, under the plausible assumptions that almost all TCE is adsorbed to the AC ($m_{HOC,adsorbed} \gg m_{HOC,dissolved}$) and that the reaction takes place at the surface, the reaction rate is determined by the Fe^0 content of the CARBO-IRON and not by the total Fe^0 concentration. The definition of symbols is as follows: $x_{Fe} = c_{Fe}/c_{AC}$ as the Fe^0 content of the AC carrier and $c_{HOC,adsorbed} \approx c_{HOC,total}/c_{AC}$ in $[\text{g}_{HOC} \text{ g}_{AC}^{-1}]$.

$$-\frac{dc_{HOC}}{dt} = k_{Fe} \cdot c_{Fe} \cdot c_{HOC,dissolved} \quad (1)$$

$$\ln\left(\frac{C_{HOC,0}}{C_{HOC,t}}\right)_{total} = k_{Fe} \cdot C_{Fe} \cdot t \quad (2)$$

$$-\frac{dc_{HOC}}{dt} = k'_{Fe} \cdot C_{Fe} \cdot C_{HOC,adsorbed} \quad (3)$$

$$\ln\left(\frac{C_{HOC,0}}{C_{HOC,t}}\right)_{total} = k'_{Fe} \cdot X_{Fe} \cdot t \quad (4)$$

Therefore, it is plausible that the reaction rate in the CARBO-IRON system is independent of the total Fe concentration applied. This is true as long as enough reductant is present for dehalogenation. In terms of longevity of the reactive particles for plume control this does not bring any advantage over pure nano-iron. However, in terms of material reduction for less extensive plumes it certainly can be beneficial. In addition, the AC carrier has a collecting function for hydrophobic pollutants such as HOCs.

The effective reach of colloidal particles in groundwater aquifers is limited. The problem is not to immobilize the particles but to hold them in suspension and provide transport lengths over several meters.



Figure 3. Mobility of the AC-based particles CARBO-IRON;
left: non-stabilized particles with $m_{mobil, (l = 75 \text{ cm})} = 85\%$ (alkaline medium)
right: stabilized with 5 wt-% humic acid resulting in $m_{mobil, (l = 75 \text{ cm})} = 90\%$ (neutral)

The mobility of the AC particles and CARBO-IRON has been examined in column tests (column length $l = 75 \text{ cm}$, $C_{CARBO-IRON} = 100 \text{ mg l}^{-1}$). Particles which passed through the column were regarded as mobile. In order to describe the mobility of the particles in the columns we defined the mobility as described in eq. (5) as an operational parameter for the column in use:

$$m_{mobile} [\%] = \frac{m_{CARBO-IRON,out}}{m_{CARBO-IRON,in}} \cdot 100 \% \quad (5)$$

Comparison of CARBO-IRON mobility to that of pure nano-iron already showed a marked increase in the transport length of the particles. However, addition of polyanionic stabilizers, such as humic acids (see Fig. 3, right column), results in longer transport lengths and a more homogeneous formation of the reaction zone. Experiments with carboxymethyl cellulose are currently in progress. First results show that carboxymethyl cellulose is able to stabilize CARBO-IRON particles even better. Both stabilizing agents are environmentally benign. Humic acids are natural materials; carboxymethyl cellulose is very inexpensive and commercially available in food grade purity.

The penetration of the reducing agent into DNAPL phases is regarded as pre-condition for source remediation. CARBO-IRON has with activated carbon *a priori* a hydrophobic carrier.

Figure 4 shows the different wetting behaviour for the more hydrophilic nano-iron particles (middle) in comparison to CARBO-IRON particles (right). The samples were slightly shaken. The figure shows the easy penetration of the hydrophobic carbon particles into the organic phase.

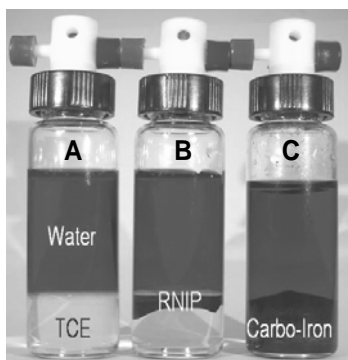


Figure 4. Comparison of wetting properties of ZVI reagents in a trichloroethene DNAPL phase under dyed water (A); (B) Reactive nano iron particles (RNIP); (C) CARBO-IRON (ZVI on activated carbon)

The effectiveness of the immobilized sorbent AC was studied, e.g. to what extent the AC barrier is available for a retardation of the dissolved pollutants. The observed retardation factor was similar to the calculated one. In contrast to the retardation potential of soil organic matter, which in similar column experiments could only be partially exploited, the sorption capacity of the AC introduced can be utilized to the full extent. This proves that the AC particles are immobilized within the favoured flow passages of the water.

4. CONCLUSIONS

Activated carbon and the composite material CARBO-IRON (ZVI on AC) are two promising materials for environmental application. Colloidal AC can form a sorption barrier and CARBO-IRON a reactive (sorption/reaction) barrier by subsurface injection.

CARBO-IRON has proved its dehalogenation activity for chlorinated and brominated C₁- and C₂-hydrocarbons in aqueous solution. Stabilizers such as polyanionic substances can help to keep the particles mobile under aquifer conditions. Humic acid as a natural product can act as a stabilizer; however, carboxymethyl cellulose is able to stabilize even higher particle concentrations of AC and CARBO-IRON and facilitates long transport distances. The hydrophobic nature of CARBO-IRON permits its distribution in NAPL phases where dehalogenation can be performed by the reactive component ZVI without the application of additives. This is a great advantage over pure nano-sized ZVI, which requires additives for source treatment. The surface properties of the novel bi-functional colloids are the basis for their possible utilization in both plume *and* source treatment - conventional ZVI does not have these properties, which can otherwise only be provided by expensive chemical additives.

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