

Nano-Catalysts and Colloidal Suspensions of Carbo-Iron for Environmental Application

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ABSTRACT

The present paper shows two different examples for *ex-situ* and *in-situ* water treatment using nano-sized materials. Two novel colloidal particles have been developed and tested in initial studies for i) the *in-situ* generation of sorption/reaction barriers based upon zero-valent iron on sorption-active carbon carriers (carbo-iron) for application in subsurface water treatment and ii) the selective catalytic elimination of halogenated hydrocarbons using Pd on magnetic carriers as agent for *ex-situ* waste water treatment.

The common ground for both applications is the utilization of nano-particles for dehalogenation reactions in the aqueous phase in order to minimize mass transport limitation and therefore permit high decontamination rates. These water treatment applications have been selected for presentation in order to show the wide applicability of nano-sized materials in environmental technology.

Keywords: zero-valent iron, carbo-iron, dechlorination, Pd catalyst, sorption-assisted reaction, water treatment

1 INTRODUCTION

During the last ten years, intensive research has been carried out on the development of suitable materials for reactive barriers in subsurface application. Permeable reactive barriers (PRBs) on the basis of zero-valent iron have already been constructed at more than 120 sites worldwide and count as an approved technology [1]. The halogenated organic compounds (HOCs) are removed from the groundwater according to the equation: $R-X + Fe^0 + H_2O \rightarrow Fe^{2+} + R-H + OH^- + Cl^-$.

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 nano-sized zero-valent iron (ZVI) to migrate in groundwater to form a reactive zone have stimulated the research on nano-particles [2].

Literature studies on nano-sized ZVI reveal on the one hand desirable properties such as high reactivity and injectability. On the other hand, undesirable properties are also described, such as a tendency to agglomeration and untimely sedimentation and hence a limited mobility under aquifer conditions [3]. The hydrophilic nature of the iron surface makes it not well suited for source remediation.

The utilization of hydrophilized carriers or poly(acrylic acid) helped to mobilize colloidal suspensions of ZVI [3].

The addition of emulsifying substrates forms emulsion droplets which contain the ZVI particles in water surrounded by an oil-liquid membrane. Emulsified zero valent iron (EZVI) has been successfully tested in a field-scale demonstration [4]. EZVI proved miscible with the organic phase; therefore, contact between the reaction partners was realized. Nevertheless, the addition of chemicals to the reactive agent is necessary in order to achieve the close contact between the reactants. In addition, the emulsified particles show even less mobility.

The objective of our work is to develop materials with tailored properties for *in-situ* generation of sorption/reaction barriers for subsurface water treatment at low cost and without the need for additional chemical supply. The surface properties should be suitable for both plume and source treatment.

ZVI in every form and particle size has its limitations concerning the pollutant spectrum which can be treated; e.g. iron completely fails for the dehalogenation of aromatic substances, such as PCBs, halogenated benzenes and phenols. However, the utilization of catalytic hydrodehalogenation with Pd catalysts can solve this problem. Palladium catalysts have proved to be well suited for promoting hydrodehalogenation reactions in the aqueous phase according to the equation $C_1H_mX_n + n H_2 \rightarrow C_1H_{m+n} + n HX$ [5]. The present paper aims at a treatment technique designed for special industrial wastewater contaminated with only small amounts of halogenated hydrocarbons – amounts which are nevertheless large enough to make a discharge into municipal sewage works impossible. The consequence is the necessity of expensive and energy-intensive incineration of aqueous waste. Therefore, especially for medium-sized enterprises, a decentralized selective wastewater dehalogenation treatment brings not only ecological credibility but also an important economic advantage.

Our research in the field of *ex-situ* water treatment follows the aim of detoxifying the water by a *selective* destruction of the HOCs in reductive hydrodehalogenation reactions on nano-catalysts containing palladium. By detoxification we mean that the persistent HOCs are converted into dehalogenated organic compounds which can easily be removed by biodegradation in a wastewater treatment plant.

2 EXPERIMENTAL

Carbo-iron. The support material activated carbon (AC, e.g. SA Super from Norit), was ground in the presence of deionized water (horizontal mill 200 AHM, Alpine

Hosokawa). 500 g of this AC ($D_{50} = 0.8 \text{ m}$, $D_{90} = 1.6 \text{ m}$) and 1080 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (= 150 g Fe^{3+}) were mixed in 1 L of water and shaken. The water was removed and the re-ground residue was reduced at 550 to 580°C under H_2 atmosphere for 8...10 h. Before application as a dehalogenation agent, the freshly produced carbo-iron was subject to a mild deactivation step. In water, carbo-iron can easily be extracted from unwanted by-products by magneto-separation. The Fe^0 content of the composite material was 20 wt-% (measuring the H_2 evolved by GC/WLD after addition of a stoichiometric excess of HCl).

Pd/Fe₃O₄. The magnetite particles (Aldrich, 20-30 nm) were spiked in aqueous solution with Pd in the form of $\text{Pd}(\text{ac})_2$. After decolorization of the orange solution (visible after magnetoseparation), H_2 treatment ensured complete reduction to Pd^0 . The catalysts contained 0.1 wt-% Pd.

Dehalogenation studies. The dehalogenation activities of both types of particles were studied in batch and column experiments using probe HOCs such as carbon tetrachloride, trichloroethene, 1,2-dibromoethene and, for the catalytic reaction, also chlorobenzene. Kinetic studies were carried out by following the educt disappearance and the product evolution (HOCs by total extraction and GC/MS analysis of the extracts; methane, ethene and ethane by analysis of headspace concentrations, and halogenide by IC analysis of the reaction solution).

3 RESULTS AND DISCUSSION

Carbo-iron. Based on approved methods in abiotic water treatment by PRBs (pollutant sorption and pollutant destruction by chemical reaction) this study focused on AC as sorbent and ZVI as reactant. 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.

Because pure nano-iron is neither sufficiently mobile nor well-suited for source remediation, we decided to follow an alternative approach. This approach is based on finely-ground AC with a D_{50} particle size of 0.8 m which is quasi-soluble, forming stable colloidal solutions in water over a wide concentration range. We gave this material additional reactivity by impregnating it with iron salts then reducing it at elevated temperatures with hydrogen. The procedure results in AC with ZVI 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.

Figure 1 shows that both components (AC and Fe^0) 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 (SAD) pattern study of the Fe particles (e.g. the larger black areas on the right-hand side of the picture) prove the crystallinity of those Fe^0 particles.

Our concern was that a close contact of AC and Fe^0 does not automatically mean that hydrophobic substances

which are sorbed to the AC carrier are easily available for reduction at the Fe centers. However, dehalogenation experiments using carbon tetrachloride, trichloroethene, 1,1,1,2-tetrachloroethane and 1,2-dibromoethene proved the suitability of carbo-iron as dehalogenation agent in the aqueous phase.

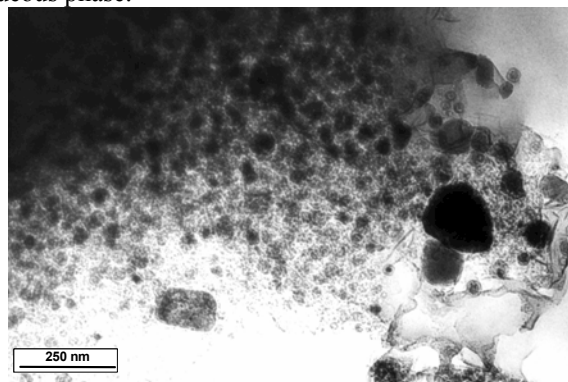


Figure 1: Transmission electron microscopy (TEM) bright-field image of carbo-iron (20 wt-% Fe^0)

Pure nano-sized ZVI can be produced by reduction of iron precursors using NaBH_4 in aqueous solution (Fe^{B}) or H_2 in the gas phase at elevated temperatures (RNIP). The differences between these two types of nano-particles concerning structural properties and reactivity in dehalogenation reactions of HOCs have been intensively studied [6,7]. The chemical nature of the iron surface was found to be very important for the particle reactivity (B-doped surface versus predominantly Fe oxide shells). Magnetite shells are believed to hinder the electron transfer from the iron to the HOC [7]. The synthesis of carbo-iron is similar to the RNIP production. Therefore, particular attention was turned to a mild deactivation step avoiding the formation of a retarding magnetite shell around the Fe nano-structures. According to our experience the deactivation step is very important for the reactivity and longevity of the ZVI.

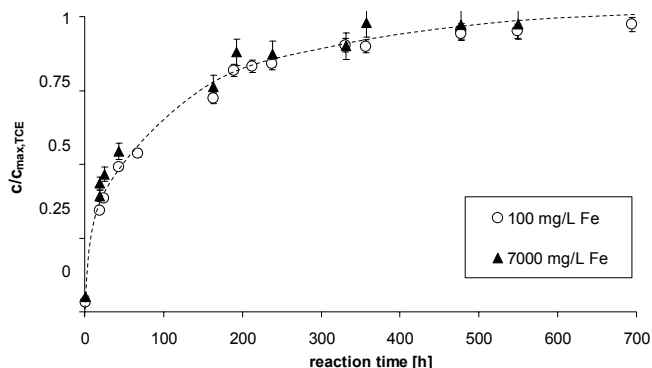


Figure 2: Observed reaction kinetics for the dechlorination of trichloroethene to ethene/ethane using various concentrations of carbo-iron. ($C_{0,\text{TCE}} = 30 \text{ mg L}^{-1}$, 0.1 M $\text{NH}_3/\text{NH}_4^+$ buffer, yields: $C_{\text{max,chloride}} = 100\%$, $C_{\text{max,C2 hydrocarbons}} = 40...45\%$)

In the batch experiments all of the mentioned HOCs were dehalogenated in a manner comparable to using pure nano-ZVI. The observed reaction rate using $7\text{ g L}^{-1}\text{ Fe}^0$ was in the same order of magnitude as known from the suspensions of conventional nano-iron with the same Fe concentration. However, the reductive dehalogenation takes place with a comparable 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.

Equations (1) to (4) show, that under the plausible assumptions that almost all TCE is adsorbed on the AC ($m_{\text{HOC,adsorbed}} \gg m_{\text{HOC,dissolved}}$) and that the reaction takes place on the surface, the reaction rate is determined by the Fe^0 content of the carbo-iron and not by the total Fe^0 concentration, with $x_{\text{Fe}} = c_{\text{Fe}}/c_{\text{AC}}$ as the Fe^0 content of AC carrier and $c_{\text{HOC,adsorbed}} \approx c_{\text{HOC,total}}/c_{\text{AC}}$ in $[\text{mg}_{\text{HOC}}\text{ g}_{\text{AC}}^{-1}]$.

for ZVI:

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

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

for carbo-iron:

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

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

Therefore, it is plausible that the reaction rate in the carbo-iron is independent of the Fe concentration applied as long as enough reductant is present. In terms of longevity in plume control this does not bring any advantage over pure nano-iron, but in terms of material reduction for less extensive plumes it certainly can. In addition, the AC carrier has a collecting function for hydrophobic pollutants.

The mobility of carbo-iron has been examined in column tests (column length $l = 75\text{ cm}$, $c_{\text{carbo-iron}} = 100\text{ mg L}^{-1}$). 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 an operational parameter:

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

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.

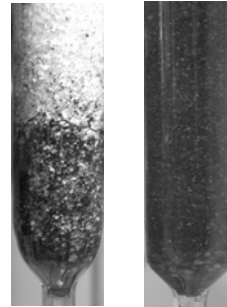


Figure 3:
Mobility of carbo-iron
Left: unstabilized particles with $m_{\text{mobil}, (l=75\text{ cm})} = 85\%$
Right: stabilized with 5 wt-% humic acid resulting in $m_{\text{mobil}, (l=75\text{ cm})} = 90\%$.

The penetration of the reducing agent into DNAP 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.

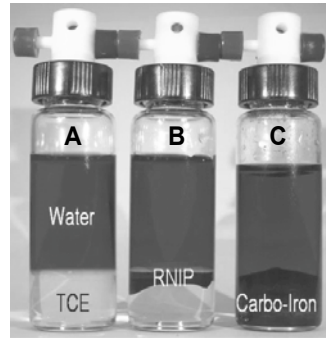


Figure 4:
Comparison of wetting properties of ZVI reagents in a TCE DNAPL phase under dyed water (A) (B): Reactive nano iron particles (RNIP, from Toda Kogyo Corp.) (C): Carbo-iron (ZVI on activated carbon)

Pd/Fe₃O₄ nano-particles. Let us come back to the other example of the application of nano-particles for environmental technology: the *ex-situ* water treatment using Pd catalysts. The specific catalyst activity can be expressed as follows

$$A_{\text{Pd}} = \frac{V_{\text{water}}}{m_{\text{Pd}} \cdot \tau_{1/2}} = \frac{\ln(c_{t1}/c_{t2})}{\ln 2 \cdot c_{\text{Pd}} \cdot (t_2 - t_1)} \quad (6)$$

(in $[\text{L g}^{-1}\text{ min}^{-1}]$)

with V_{water} as the water volume applied, m_{Pd} and c_{Pd} as the Pd mass and concentration and $\tau_{1/2}$ as the HOC's half-life, obtained from its disappearance kinetics. t_1 and t_2 are two arbitrarily chosen sampling times; c_{t1} and c_{t2} the corresponding HOC concentrations [8]. The value of $A_{\text{Pd},i}$ is equivalent to a first-order rate coefficient according to $k_{\text{obs}} = \ln 2 \cdot A_{\text{Pd},i} \cdot c_{\text{Pd}}$ $[\text{s}^{-1}]$. Equation (6) helps to evaluate the effectiveness of Pd catalysts. Pd activities of $0.1\text{ L g}^{-1}\text{ min}^{-1}$ were found in field tests for groundwater treatment using granular Pd catalysts such as Pd on γ -alumina [9].

However, the inherent Pd activity is higher by several orders of magnitude. The catalytic activity of the described particles for model HOCs such as chlorobenzene or TCE is extremely high: up to 3000 L/(g_{Pd} min). This is several orders of magnitude higher than can be achieved in fixed-bed arrangements of granular catalysts for groundwater treatment. If in environmental applications only a fraction of this reactivity can be reached, Pd catalysts will eventually make their way into environmental technology as an approved tool.

We regard magnetite particles as attractive carriers when adding hydrogen or other hydrogen sources because they are quite resistant against various milieu parameters. Hydrogen has a water solubility of $S_{H_2}^{15^\circ C} = 0.84 \text{ mM}$ at $p_{H_2} = 100 \text{ kPa}$. This may be insufficient for the treatment of highly contaminated wastewaters. For example, from the stoichiometry of the hydrodechlorination reaction it follows that only up to 28.6 mg L^{-1} of trichloroethene can be reduced with dissolved hydrogen ($C_2HCl_3 + 4 H_2 \rightarrow C_2H_6 + 3 HCl$). In practice, however, much higher HOC concentrations may occur. Formic acid as an alternative H-source was found to be as reactive as H_2 under acidic conditions, but less reactive under alkaline conditions. In the framework of our studies in the field of wastewater treatment using nano-sized catalysts for clean-up of HOC-contaminated wastewater, formic acid has already been tested and found to be suitable as a H-donor. Nano-sized Pd-magnetite catalysts can even be stored as a suspension in formate solution ($pH > 8$) without loss of activity. This mixture can be seen as part of a wastewater-treatment toolkit. Studies involving other H-donors are in progress.

The catalytic material was tested with various technological options, including batch and continuous flow reactors, depending on the type and amount of wastewater to be treated. The performance of a laboratory flow-through reactor revealed a Pd activity of $> 3000 \text{ L/(g min)}$.

The extraction of the magnetite particles from the reaction suspension by means of magnetoseparation was highly effective. The results of the laboratory tests are altogether very promising.

Due to the fact that catalysts in the nano-scale are still novel tools in water treatment, it is necessary to characterize and evaluate both their potential and any possible risks they may pose. The particle size not only determines the catalytic activity; it may also be possible for such tiny particles to pass through cell membranes, which bears the threat of their possible chemical reactions with cell constituents. Therefore, investigations concerning size-dependent cell toxicity of various types of nano-catalysts are necessary. The chemical potential of such reactive systems is enormous, but it can only be exploited responsibly on the basis of a thorough ecotoxicological analysis of possible risks in the framework of an interdisciplinary approach. The evaluation of the risks of such nano-particles for living cells plays an important role within the presented studies; of course we hope that the benefits will be found to outweigh the potential risks.

4 CONCLUSIONS

With carbo-iron (20 wt-% ZVI), a novel material is provided which forms stable colloidal solutions up to high concentrations and Ca^{2+} concentrations. Stabilizers such as polyanionic substances can help to keep the particles mobile under aquifer conditions. Humic acid as a natural product can act as stabilizer; however, carboxymethyl cellulose is able to stabilize much higher particle concentrations of carbo-iron and facilitates long transport distances.

Carbo-iron has proved its dehalogenation activity for chlorinated and brominated C_1 - and C_2 -hydrocarbons in aqueous solution. Furthermore, the hydrophobic nature of carbo-iron permits its distribution in NAPL phases where dehalogenation can be performed without the application of additives. This is a great advantage over pure nano-sized ZVI, which requires additives for source treatment.

Extremely active catalysts for cyclic batch applications can be produced on the basis of ferromagnetic nano-sized carrier colloids containing only traces of Pd (0.1 wt-%). Nano-sized Pd catalysts have been successfully tested for waste water problems at the laboratory scale. Dehalogenation using pure Pd colloids or Pd on colloidal supports shows the true inherent activity of Pd clusters which is several orders of magnitude higher than reached in fixed bed arrangements due to minimized mass transfer limitations. Magnetite particles are suitable catalyst carriers because of their high resistance against milieu parameters. Their magnetism allows a complete extraction of the nano-particles from the treated water by magneto-separation. Beside the study of the opportunities and the high potentials of such catalyst systems, another objective of our work is an evaluation of their environmental risks.

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