REDOX PROPERTIES OF IRON-BASED MATERIALS IN WATER TREATMENT TECHNOLOGIES: AN OVERVIEW OF LABORATORY VERSUS FIELD EXPERIENCES

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ABSTRACT

In this paper, iron-bearing compounds where the iron atoms are in different oxidation states (i.e. metallic iron on one side and superoxide with iron VI on the other side) are introduced and their applicability for water treatment is clearly demonstrated. The versatility of iron atoms in various forms (mainly in variable oxidation states) could cover broad range of water treatment technologies (reduction, sorption, oxidation, and combined technologies even in relation to biotechnologies and other physical fields – electric and/or magnetic) when iron is in reduced (Fe0), oxidized (FeII,III), or superoxide (FeIV,V,VI) state, respectively. Thus, they could cover treatment of broad range of pollutants (organic compound like TCE, PCE, DCE, BTEX; inorganic compounds including heavy metals, CrVI, arsenic, metal cyanides, nitro-compounds; as well as emerging contaminants from the broad family of pharmaceuticals, endocrine disruptors, pesticides and herbicides). Such technologies proved to be well applicable and cost-effective in many cases, environmentally-friendly with formation of non-toxic iron oxides (i.e. environmentally benign product with sorption/coagulation properties and also magnetic properties allowing magnetic separation of reaction products from the treated media) representing, thus, competitive alternative to conventional water-treatment technologies. The high potential of the presented technologies lies mainly in the restoration of polluted groundwater and soil environment, waste- and surface-water treatment, as well as in the treatment of drinking water where fast and highly-efficient elimination of particular compounds and/or microorganisms is a key parameter.
Keywords: zerovalent iron, nanoparticles, ferrate(VI), iron oxides, water treatment, redox reactions, laboratory experiments, pilot tests, oxidation, reduction.

1 INTRODUCTION

Removal of persistent and emerging organic and inorganic pollutants is a challenging task for advanced water treatment techniques. Especially crucial are the time and economical sustainability of remediation and achievement of contamination limits. This is particularly concerning polluted sites, e.g. groundwater impacted by the acid mine drainage and by the industrial or pharmaceutical activities, groundwater within the former military zones, surface and drinking water contaminated by microorganisms, P, As, drugs, pesticides, endocrine disruptors, etc. The innovative nanomaterials are beneficial to this purpose because of their high reactivity (especially metallic nanoparticles [1]) and sorption capacity (metal oxide nanoparticles [2]). The iron based materials proved to be promising material due to the availability of iron-bearing precursors and versatility of Fe in its various oxidation states while Fe0/II is a reducing agent [3], FeIV/V/VI is a strong oxidant [4]. Furthermore, the non-toxic iron oxyhydroxides are the final reaction products of Fe-based (nano) materials [5], [6]; these minerals show the similar properties as their naturally occurring analogues [7]. However, the kinetics and reaction mechanisms of contamination removal by the (nano)materials differ under laboratory and real environmental conditions. The main reason of such variation is a hardly reachable simulation of complex real water chemistry. Another difficulty is a presence of sediment (rock bed) in case of groundwater remediation, and that

can strongly influence behaviour of Fe0 nanoparticles when removing chlorinated hydrocarbons.

The main aim of this presentation is to reveal the results of reactivity studies performed on the (nano) materials developed in Regional Centre of Advanced Technologies and Materials. These include particularly *(i)* nanoscale zero-valent iron (nZVI) particles, a material suitable for reductive groundwater remediation, *(ii)* nZVI on carbon matrix composites, a technology combining reduction and sorption, *(iii)* iron oxides, the efficient sorbents used in surface and wastewater treatment and *(iv)* ferrates (FeIV/V/VI), strong broad-spectrum oxidizing agents. The reactivity of above mentioned materials towards various contaminants (laboratory tests employing organics - chlorinated hydrocarbons – as well as inorganics – Cr, As, Cu, P and cyanides) will be demonstrated. In addition, the results of pilot applications of identical nanomaterials (produced by NANOIRON, s.r.o.) will be presented.

2 NANOTECHNOLOGY FOR WATER REMEDIATION

There are three major water systems whose remediation represents a challenging task and that are usually treated using conventional long-term verified methods.

Freshwater contamination is generally closely related to the sewage release due to the fact the rivers and lakes are primary recipients of household and industry effluents. Other sources of freshwater contamination can be polluted rainwater or fertilizers run-off from the fields. The most noticeable and emerging sign of freshwater pollution is fish mortality. Both, freshwater and groundwater can serve as a source of drinking water.

The latter one is even more sensitive to increased contamination levels, especially because subsurface aquifers are the last stage in recipient hierarchy. Among major types of groundwater contaminants belong volatile organic compounds (VOCs), namely trichloroethylene (TCE) and tetrachloroethylene (PCE). The main sources of such contamination are usually containers and open reservoirs serving as stores of chemicals, products or waste that leak into the subsurface [8].

Wastewater is a special type of water system due to its increased content of solid particles and suspended matter. The wastewater treatment is basically focused on organic carbon, nitrogen, phosphates and heavy metals removal. Another important factor necessary to monitor (and fulfil its concentration limit) is a biological contamination - therefore the final hygienization of treated water is needed [9].
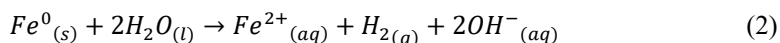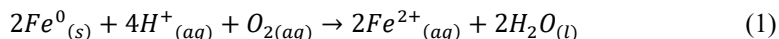
There are many advantages of nanomaterials that make them suitable for various types of polluted waters. In contrast to the conventional technologies, innovative water treatment methods show enhanced reactivity and greater surface area, they are environmentally-friendly and can be modified in order to profit from combined/synergistic effects of hybrid materials [10].

3 REDUCTIVE ACTION OF ZEROVALENT IRON NANOPARTICLES

More than twenty years ago, technologies based on redox properties of zero-valent iron (ZVI), i.e., macro-/microscale and later also nanoscale, turned out to be highly promising in technologies of groundwater and soil remediation. Since that time, chemical behaviour of ZVI in the environment was studied in detail and contamination removal capability of Fe^0 was associated with its ability to donate electrons while oxidized to FeII/FeIII. The acceptors of these electrons can be a wide range of pollutants undergoing parallel reduction (e.g. chlorinated hydrocarbons, CHCs, or metals). According to the same mechanism, ZVI reacts with water and dissolved oxygen as well and this causes a subsequent increase in pH (see eqns 1 and 2) [11]. Among chemical reduction, adsorption of contaminants onto

the surface of ZVI transformation products (ferric oxyhydroxides) plays a key role in remediation processes [12].

$$2Fe^0_{(s)} + 4H^+_{(aq)} + O_{2(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \qquad (1)$$

$$Fe^0_{(s)} + 2H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)} + 2OH^-_{(aq)} \qquad (2)$$

As evident from ZVI chemical properties described above, enhancement of ZVI reactivity and surface area results in improved removal efficiency. NZVI particles are more reactive and shows greater surface area-to-volume ratio and therefore showed to be more efficient when used as a macro/microscale ZVI equivalent [10].

Generally, nZVI particles consist of a metallic core and an oxidic shell as displayed in Fig. 1. They tend to aggregate due to the van der Waals attraction on their surface, and settle down over short time [13]. A surface stabilization of nanoparticles is performed in order to eliminate nZVI aggregation, thereby increasing their migration in the subsurface. There are many surface stabilizers currently used such as guar gum, carboxymethyl cellulose and polyacrylic acid [1].

A first pilot application of nZVI was performed by D. W. Elliott and W. Zhang in New Jersey in 2001. An injection of bimetallic nanoparticles (Fe^0/Pd^0) reduced CHCs contamination by 96% [14]. Since then, usefulness of remediation techniques based on nZVI was proved by their successful pilot- and full-scale application in USA as well as in Europe [15]. In Czech Republic, not only pilot injections but also successful full-scale remediation events employing nZVI were documented [16]. Moreover, this technology has been demonstrated within the 7FP NanoRem project (see www.nanorem.eu) at several sites differing in contamination and hydrogeological conditions.

4 OXIDATIVE ACTION OF FERRATES (VI)

Currently, considerable attention is devoted also to utilization of ferrate compounds in water treatment studies. Ferrate is high valent iron-oxyanion including Fe(VI), Fe(V) and Fe(IV). The second and third is very unstable in water solution and easily react to Fe(IV) and Fe(III) compounds. Conversely, water decomposition of Fe(VI) is significantly slower and in dilute solutions the highest stability is in pH range 9.4–9.7 or under strong alkali conditions. Contrary to above-described nZVI particles with strong reductive effect, ferrate ion $(FeO_4)^{2-}$ is very strong oxidant. Under acidic condition the redox potential of ferrate(VI) is 2.20 V,
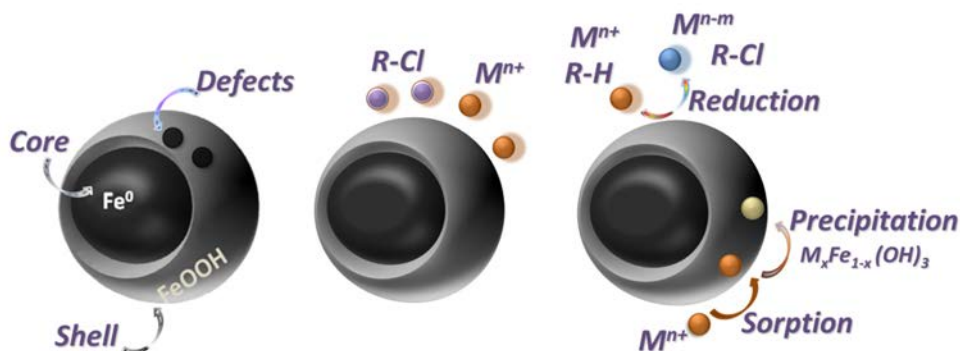

Figure 1: Structure of nZVI particle and scheme of its reactivity towards CHCs and metals.

the strongest of all oxidants used in water treatment [17]. In alkaline solution, the redox potential reaches 0.70 V. Potassium ferrate (K_2FeO_4) belongs to the most studied among the family of ferrate(VI) derivatives, because it is relatively stable and easily prepared. It is insoluble in organic solvents and rapidly reacts to Fe(III) compounds and oxygen in strong acids. Degradation of various pollutants was successfully tested involving pharmaceuticals [18], endocrine disruptors [19], organosulfur compounds [20], pesticides [21], chemical warfare agents [22]. Furthermore, inorganic compounds such as amines [23], cyanides [4] and heavy metals [24]; were investigated with respect to removal by ferrate(VI). In addition to the high efficient removal of pollutants, ferrate(VI) can effectively eliminate water pathogens, bacteria and viruses and acts as disinfection agent [25]. Additional advantage is that all ferrate species (IV, V, VI) belongs to environmentally friendly oxidants. Consequently, reaction products in the form of trivalent iron compounds are non-toxic and can serve as coagulant or flocculant to remove non-degradable pollutants. Ferrate(VI) does not react with bromide ion to resulting carcinogenic bromate ion and it was examined as an alternative to chlorine for the disinfection of water.

5 REACTIVITY OF SELECTED NANOPARTICLES – LABORATORY-SCALE EXPERIMNETS

The nZVI particles, both as-prepared and surface modified, are extensively tested in laboratory scale conditions prior to their application in field. For this purpose, either model solutions are prepared, or real waters from contaminated localities are collected. The most common systems for nZVI testing include Cr^{6+} (i.e., reduction of hexavalent chromium), various chlorinated hydrocarbons (i.e, reductive dehalogenation) and broad range of other metals, anions and organic compounds. In the following part, we will focus on the two most common tests – hexavalent chromium reduction and reductive dehalogenation of chlorinated compounds.

5.1 Degradation of chlorinated hydrocarbons (CHC)

The changes in the concentration of chlorinated hydrocarbons as a function of time are commonly monitored by laboratory batch experiments. The concentrations of CHC (e.g. DCE, TCE and PCE) are determined by gas chromatography in defined time intervals [26]. The reaction mixtures in separate reagent bottles (shaken) are then analyzed one by one after sufficient contact time (e.g., 2, 4, 8 and 14 days).

To simulate conditions at the particular locality, the synthetic solution of the contaminated groundwater is typically prepared by injection of methanol stock solutions into the bottles so that the final concentrations of chlorinated ethenes in the solution is close to the concentration in polluted water at. The reactions are then initiated by the addition of the nZVI dispersion to get the concentration of e.g. 1, 2 and 5 g/L.

During the experiments, the reagent bottles are shaken and after selected times, part (in the range of 5 – 10 mL) of the aqueous phase is withdrawn and immediately injected into sealed 10 mL vials [1]. The typical results of such laboratory study are presented in Fig. 2.

5.2 Reduction of Cr(VI)

Chromium is a heavy metal that is used in many engineering and chemical industries such as electroplating facilities and tannery industries [27]. It exists mainly in the oxidation states of Cr(VI) and Cr(III) [28]. It is characterized as one of the most highly toxic carcinogenic and mutagenic environmental contaminants. Chromium compounds can cause several serious
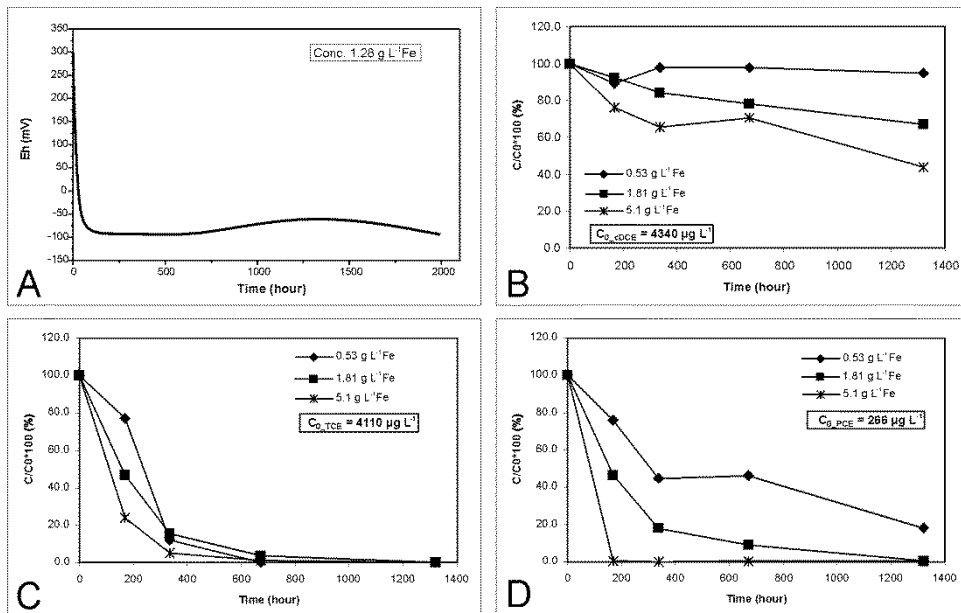
Figure 2:   Changes in Eh (A) and concentrations of cis-DCE (B), TCE (C), and PCE (C), induced by applications of nZVI at variable concentrations. (*Adapted from [26].*)

health problems like diseases to the respiratory tract, stomach and small intestine. Ions like Cr(VI) can readily accept the electrons that are provided from zero valent iron and be reduced to lower and less toxic oxidation states [29], [30]. Therefore, Cr(VI) compound is conventionally used as a model pollutant for routine laboratory evaluation of nZVI reactivity.

Cr(VI) concentrations, that is contented in water, can be determined colorimetrically by using UV-Vis spectroscopy (Fig. 3). In order to be able to detect chromium, the 1,5-diphenylcarbazide method is used that is based on the reaction of dissolved Cr(VI) with 1,5-diphenylcarbazide molecules in acid solution leading to the formation of a red−purple chromium 1,5-diphenylcarbazide complex that is measured spectroscopically at 540 nm [31], [32]. The calibration curve is initially determined by using the absorbance spectra of standard chromium solutions (Fig. 3). Diphenylcarbazide solution is prepared by dissolving diphenylcarbazide in analytical grade acetone while the pH of the solution is adjusted by phosphoric acid. The removal of chromium by nZVI addition to reaction solution is demonstrated on Fig. 4. The field data are presented and discussed in relation to bioremediation in the paper of Němeček et al. [3], and solely the effect of nZVI on Cr(VI)-contaminated groundwater is demonstrated in the paper of Němeček et al. [33].

5.3 Column experiments

Alongside the nanoparticle reactivity, the other key parameter which has to be evaluated prior to field-scale application of nanoparticles for groundwater remediation is the nanoparticle mobility in subsurface environment. The mobility of nZVI particles is commonly monitored using of laboratory columns typically made of glass allowing to visually or magnetically
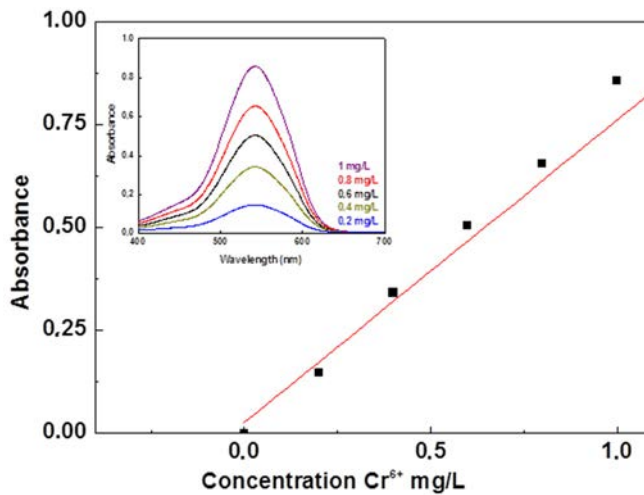
Figure 3: Absorption spectra and calibration curve for hexavalent chromium, Cr(VI).
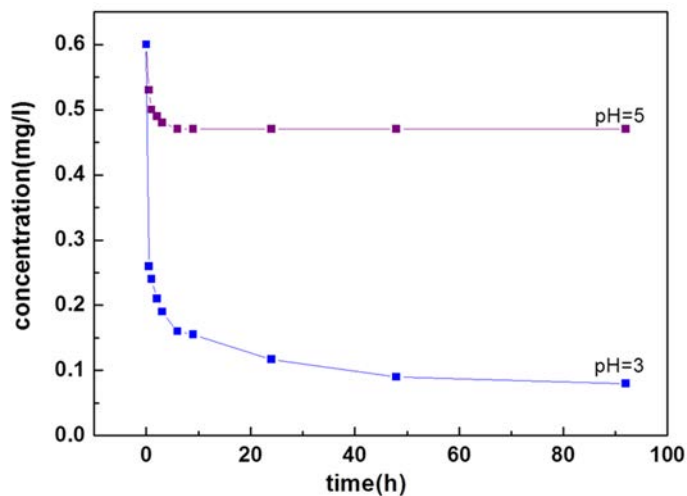

Figure 4: Removal efficiency on Cr(VI) by zero valent iron in 2 different pH values (dose of material: 1.8 mg/L of nZVI).

monitoring the particle migration within the medium [1]. Columns are filled with well-defined medium- to coarse-grained material (e.g., silica sand with a size fraction typically up to 2 mm), or sieved sediment from certain locality. The fundamental column parameters have to be determined by a conductivity, pH and ORP measurement, and also Fe-concentration (Fig. 5). The dispersion containing nZVI particles is then pumped into the columns with a peristaltic pump at the constant flow rate comparable or higher than is the groundwater flow at particular treated locality.
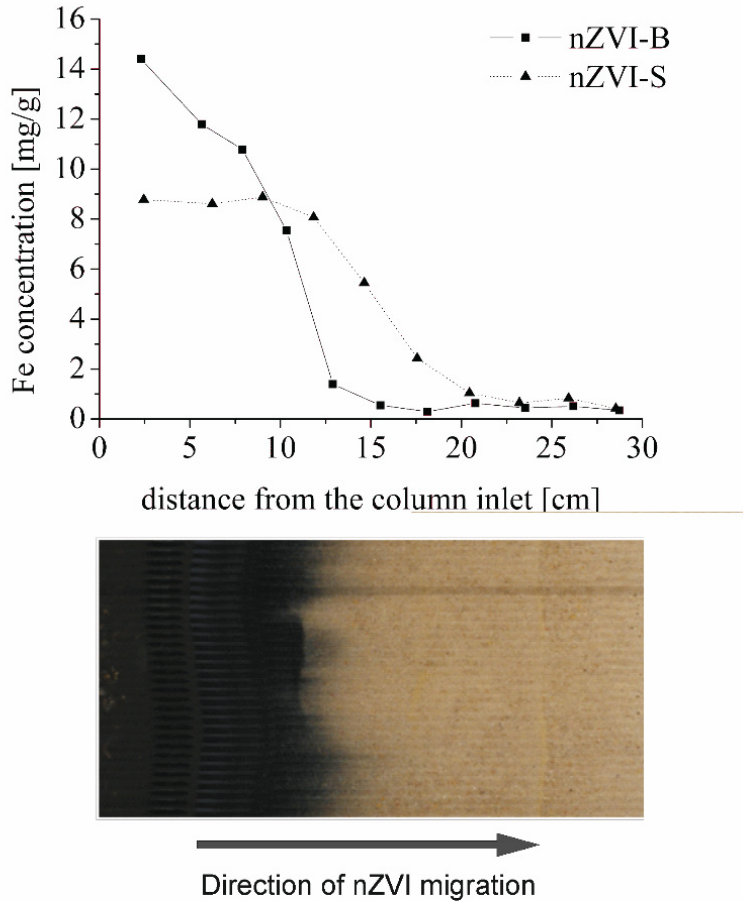
Figure 5: Example of column study of nZVI migration. Top – concentration profile of Fe over the column length, bottom – visual inspection of nZVI migration in sand-filled columns (nZVI-S – nZVI modified by Tween 80, nZVI-B - bare nZVI particles). (*Adapted from [1].*)

6 EXAMPLE OF FULL SCALE REMEDIATION

Up to the present time, there are up to 87 known sites, where nZVI particles have been applied (according to 7FP NanoRem reports, see also [15] and references therein), including 15 sites with full scale remediation (7x USA, 5x Czech Republic, 1x Canada, 1x Germany, 1x Netherlands). The remaining applications represent pilot/field tests. The pilot tests have been performed mainly in USA (41), Czech Republic (7), Germany (6), Canada (4), France (2), Denmark (2) and also in Belgium, Hungary, Israel, Italy, Portugal, Spain, Switzerland and Taiwan, where the main contaminants are mostly the chlorinated hydrocarbons (CHC), in some cases also hexavalent chromium or their combinations.

The site, chosen for the demonstration of full scale remedial application, is a former industrial complex at Horice v Podkrkonosi (Czech Republic). The contaminated site covers

the area of 150 m by 250 m [1], where the uppermost horizon of quaternary sediments is formed by loess loam (7 m) followed by sandy and silty clays (approx. 4 m) involving two aquifers with low permeability (typically 10^{-6} m²/s to 10^{-5} m²/s): the upper quaternary aquifer has the bottom of about 7 m bgs, lower Turonian about 13 m bgs. In the contaminated quaternary aquifer, groundwater is typically at the depth of about 4 m bgs. The main sources of contamination included frequent PCE spills in 1970s and 1980s [1]. Therefore, the contamination involved mainly PCE with minority of TCE, cis-DCE and vinylchloride (VC), and negligible amounts of the other hydrocarbons with total concentration of CHC up to 60 mg·L^{-1} (Quaternary aquifer) or up to 20 mg·L^{-1} (Turonian aquifer) [1]. The location of the five main contaminated spots is shown in Fig. 6 (estimated overall area of aquifer is 1500 m² and volume about 10,000 m³). For the full-scale application, the total amount of 1 ton of nZVI slurry (i.e., ca 0.2 ton of nZVI particles) was injected into 82 application wells within the most polluted parts. Right prior to application, the highly concentrated and surface-modified nZVI dispersion by TWEEN 80 was diluted at the application site to form dispersion with the final nZVI concentration of 2.5 g·L^{-1}, injected then by a direct push method (PowerProbe) at a pressure of 0.8 MPa [1].

The *in situ* application of nZVI slurry induced immediate changes in ORP, pH, and DO, being still recognizable even after 9 months. For the monitoring well, there was a decreased in ORP down to -160 mV, increase of pH up to 8-10, and the dissolved oxygen remained below 0.5 mg/L [1]. The observed decrease in the concentrations of all monitored CHC species at 5 main contaminated spots confirmed high performance of the applied nZVI particles both in Quaternary and Turonian aquifers (Fig. 6). The CHC concentrations decreased in 62% and 53% from initial values in Quaternary and Turonian aquifers, respectively. However, the low permeability of both aquifers turned out to be limiting factor for more efficient treatment, controlling the limited extent of nZVI migration over long distance [1].

Nevertheless, the contaminated areas were significantly reduced in all five monitored spots (e.g., up to 80% in Quaternary aquifer; Fig. 6). The application of nZVI had also effect on the Turonian aquifer, which was not primarily treated by the nZVI dispersion, where the reduction of the CHC contaminated areas were in the range from 37% up to 73% (Fig. 6), indicating good hydraulic communication between both aquifers [1].

7 FATE OF NANOPARTICLES USED FOR REMEDIATION

Along with detailed monitoring of changes in contamination level, any kind of nanoremediation has to be monitored in detail also in terms of potential toxicity (i.e., mainly ecotoxicity) and fate of used nanoparticles and their reaction products. When introduced into the environment, all the engineered nanoparticles (ENPs, e.g. metallic nanoparticles, metal oxide nanoparticles and carbon-based nanostructures) pose a potential risk for indigenous organisms as well as for humans. Since 2006, concerns about ENPs toxicity and environmental impact have arisen and therefore a development of analytical techniques enabling tracing of ENPs in the environment emerged [34].

An establishment of nZVI particles (and partly also ferrates) fate after their injection into the subsurface involves evaluation of their migration behavior as well as identification of their transformation products. There are some useful analytical tools serving this purpose, such as direct and indirect nZVI detection methods. Most of the methods for nZVI fate characterization are based on *in-situ* measurement of physical-chemical groundwater parameters and so they belong to the indirect techniques. This group includes e.g. ORP, pH and dissolved iron concentration measurements. Direct analytical approaches require usually sophisticated instrumentation and thus they are destined to be measured ex-situ (typically

combination of microscopic and spectroscopic techniques, X-ray powder diffraction and Mössbauer spectroscopy, etc.) [35].

During and after the application, nZVI reacts with water, dissolved oxygen and contaminants and transform into iron oxides and/or oxohydroxides subsequently enhancing remediation efficiency thanks to their high sorption capacity [5]. Moreover, these reaction products are non-toxic and they occur naturally in the environment [26].
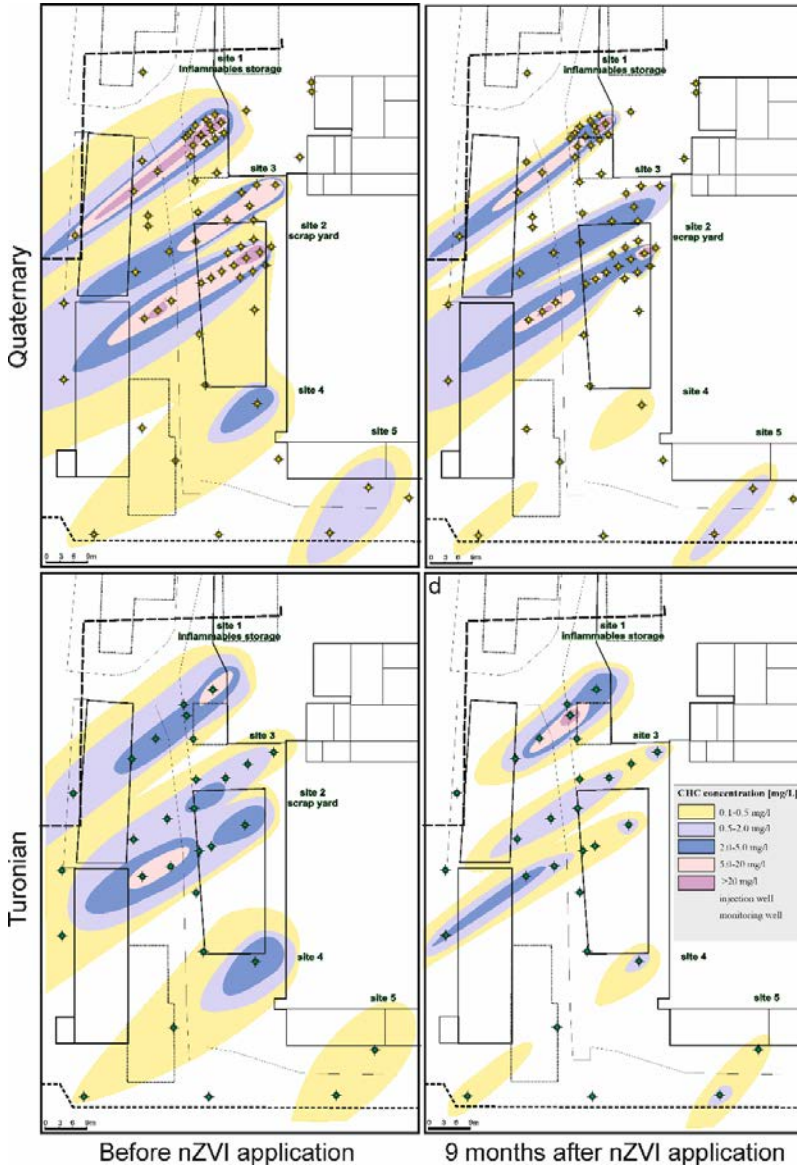

Figure 6:   Illustration of the sum of CHC concentrations in Quaternary (top) and Turonian aquifers (bottom) before and 9 months after the application of nZVI dispersion. (*Adapted from [1].*)

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