

# Nanodegradation of chlorinated hydrocarbons from groundwater in the native geological environment (laboratory batch experiment)

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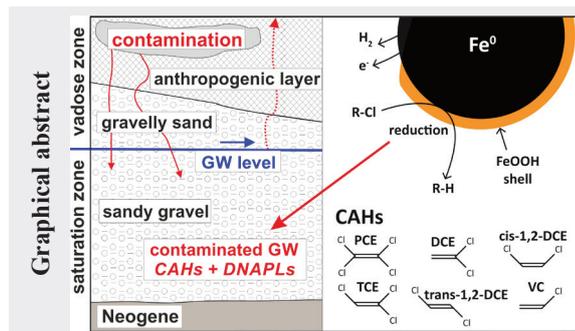
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**Abstract:** Degradation of chlorinated aliphatic hydrocarbons (CAHs) by application of nanoscale zerovalent iron (nZVI) to the geological environment represents an innovative remediation procedure. For a successful process of removing hazardous pollutants from the geological environment there is necessary to carry out experiments simulating a real geological environment in a longer series of observations. This experimental study represents the nanodegradation of chlorinated ethenes using four concentrations of synthetic nZVI from the contaminated groundwater in the simulated geological conditions of model environmental burden (non-contaminated gravel). The concentration of CAHs in the closed environment decreased even without nZVI addition, but nZVI accelerated the removal of CAHs. The complete degradation of CAHs was achieved already at the lowest concentration of nZVI – 1 g.l<sup>-1</sup>. No vinyl chloride has been determined after the nanodegradation, therefore it is assumed that the degradation pathway led to the formation of non-toxic products. The gravel attenuates the alkalization of the groundwater after the nZVI addition, giving a perspective to further *in situ* application. The concentrations of selected CAHs (*cis*-1,2-DCE, PCE, TCE and the sum of five CAHs) after degradation by nZVI were below the hygienic limits for groundwater according to Directive by the Ministry of Environment of the Slovak Republic No. 1/2015-7.

**Key words:** nZVI, nanodegradation, reduction, chlorinated aliphatic hydrocarbons, CAHs



Highlights

- Nanodegradation of chlorinated aliphatic hydrocarbons (CAHs) from the native contaminated groundwater is proposed.
- Nanoiron particles readily degrade CAHs by the mechanism of reduction
- The impact of the native geological environment on the CAHs nanodegradation is explored
- Results show the great potential for *in situ* application of nanoremediation technique

## Introduction

The group of chlorinated aliphatic hydrocarbons (CAHs) belongs to the most significant environmental contaminants. They are widespread and pose a health risk already at low concentrations (Barbee, 1994). CAHs are less soluble in the water, but soluble enough to migrate through the flow of groundwater over long distances with ability to contaminate the ecosystems, which haven't been contaminated primarily (Yu & Chou, 2000). The contamination of the environment with the chlorinated hydrocarbons is the result of release into the soils and waters during their production and application, originating during the years, when its potential toxicity was no

priority. Chlorinated hydrocarbons are considered toxic even at the concentration of 5 µg.l<sup>-1</sup> due to their potential carcinogenicity (Schiefler et al., 2018).

### The fate of CAHs in the environment

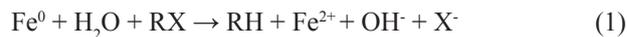
This study deals with chlorinated ethenes: vinyl chloride (VC), 1,1-dichloroethylene (DCE), *cis*-1,2-dichloroethylene (*cis*-1,2-DCE), *trans*-1,2-dichloroethylene (*trans*-1,2-DCE), trichloroethylene (TCE), perchloroethylene (tetrachloroethylene, PCE) and their removal from the groundwater with nanoscale zerovalent iron particles (nZVI) in microcosm. CAH solvents are important industrial agents used for degreasing of metals, cleaning electronic components, dissolution of rubber, removing of

oil and wax from fibers, and dry cleaning of fabrics (Bhatt et al., 2007). CAHs are used as extracting agents for fish meal, leather, oil-containing seeds, soy, coffee beans, and are important intermediates in manufacturing, especially for polyvinyl chloride (PVC) production (Barbee, 1994). Generally, the most common exposition way of CAHs is the inhalation of the contaminated air and the dermal contact with the polluted material. After ingestion, VC is transformed to the high-reactive epoxide chloroethylene-dioxide, which converts to chloroacetaldehyde and binds to DNA, therefore it is considered mutagenic. Acute poisoning with VC occurs up to a concentration of 20–50 mg.l<sup>-1</sup> with irritation of the respiratory tract and eyes. Chronic poisoning lead to “vinyl chloride disease” – summary name for the headache, liver damage, and pulmonary fibrosis, not excluding carcinoma of liver, lungs, digestive tract and brain (Frankovská et al., 2010). Breating of high concentrations of 1,2-DCE may cause nausea, vertigo, drowsiness, weakness, tremor and fatigue. Chronic exposure to TCE may cause kidney and liver cancer, the non-Hodking lymphoma, and also poses a potential hazard for noncancer toxicity to the central nervous system, immune system, male reproductive system, and the developing embryo/fetus (Chiu et al., 2013). PCE inhaled at the high concentration may be toxic to the central nervous system, liver and kidneys, the carcinogenity was proved on many animal studies, but in relation with human body, it is still a probable carcinogen (Mundt et al., 2003). Among chlorinated ethenes, only VC and TCE are classified as carcinogenic to humans by all routes of exposure (Group A) by US EPA (Rusyn et al., 2014; Walter et al., 2011).

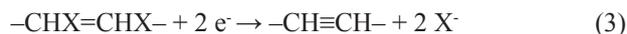
#### *Nanoiron as the tool for CAHs degradation*

Based on the chemical structure of CAHs, they are predestinated for reductive degradation, therefore one of the best options for their removal is the nanoiron. Iron is well-known due to its reduction abilities. When transferred into the nano-dimensions, iron acquires new features and properties: greater specific surface, higher concentration of reactive sites, stronger reduction capability, higher reactivity through the whole range of contaminants, including CAHs, and better mobility in the matrix. One of the most critical limitations of the use of nZVI is their tendency of agglomeration into the clusters, therefore it is recommended to provide the surface modification of nZVI, or addition of substances increasing their mobility (Stefaniuk et al., 2016; Tian et al., 2000). The options for preventing the unwanted agglomeration, passivation, and sedimentation of nZVI is covering of the nZVI particles with a layer of stabilizing compound that may cause the changes in surface charge and decrease their aggregation. The most used compounds are (bio)polymers, anionic surfactants, starch, carboxymetyl cellulose (CMC), guar gum, and polyacrylic acid. Another type of stabilization is

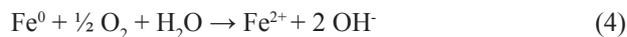
the emulsification of nZVI, where nanoiron particles pass to the hydrophobic medium. Encapsulation into the matrix and immobilization on the surface of matrix solves the problem of difficult separation from the remediation zone (Stefaniuk et al., 2016). CAHs are nanodegraded mainly by the mechanism of adsorption and reduction (Eq. 1),



where R is the hydrocarbon chain and X halogen. In the aquatic environment, zerovalent iron oxidizes from Fe<sup>0</sup> to Fe<sup>2+</sup>, while releasing electrons, which is crucial for contaminant reduction. Depending on the type of hydrocarbon, the reaction can run by the mechanism of sequential hydrogenolysis (Eq. 2), taking place in the strong reductive conditions, or by reductive β-elimination (Eq. 3), which occurs when two vicious carbons in the chain are substituted by chlorine, resulting in the release of halogen as halide.



When there is a high concentration of dissolved oxygen in the water, another mechanism of action is proposed (Eq. 4). With a decreasing concentration of O<sub>2</sub>, the redox potential drops into the anoxic values. In this case, groundwater reacts with iron by the process of corrosion with hydrogen depolarization (Eq. 5), with the formation of hydrogen, which stimulates the growth of anaerobic microorganisms with the ability of dehalogenation of contaminants. Regardless of aerobic or anaerobic dehalogenation, in the result, there is an increasement in the OH<sup>-</sup> concentration, accompanied with the pH increase. In this case, it is possible to buffer the environment with solubilized CO<sub>2</sub> or by the addition of bicarbonates (Černík, 2010).



From the above-mentioned mechanisms, the most common pathway of CAH degradation via nZVI is a reduction, mainly α- or β-elimination. The observed products of PCE and TCE reduction include *cis*-1,2-DCE and VC (Wacławek et al., 2015). CAHs may be degraded in the natural biological environment, as well. The degradation kinetics of all biological reactions are complex and might depend on several biochemical and environmental factors. Generally, it is a first-order decay, when the biodegradation rate is primarily a function of the CAH concentration.

A conceptual anaerobic-aerobic model for biological reactions of CAHs is proposed PCE is assumed to degrade

only via the anaerobic pathway, the less-chlorinated CAHs can be degraded by both—anaerobic and aerobic mechanisms even to ethene (Clement et al., 2000). Nanodegradation of various hazardous substances is still a subject of current interest, but recently the research is focused on improving of remediation efficiency by a combination of nZVI with another physico-chemical or biological technique. PCE from artificially contaminated medium was completely removed after 6 days of simultaneous application of anaerobic microbial consortium and nZVI modified by layered double hydroxide (Wang et al., 2020). Bimetallic FePd nanoparticles incorporated in the pores of granular activated carbon was synthesized by Zhang et al. (2017) and integrate the mechanisms of reduction and absorption with 100 % removal efficacy in microcosm. The combination of nZVI stabilized with polyvinylpyrrolidone and surfactants (CTAB, SDS) enhanced the PCE degradation resulting in complete removal of TCE from the soil-water system within 3 hours (Tian et al., 2020). Application of nZVI (Nanofer 25S) and bacterial strain *Ochrobactrum anthropi* isolated from the contaminated sediment has been shown to be effective in removing of polychlorinated biphenyls (PCBs) with 99 % degradation of Delor 103 – industrial mixture of PCBs (Horváthová et al., 2019).

Taking into the account the further *in situ* application of nZVI, the toxicity of nZVI towards various trophic levels should be considered. When introduced into the environment, bacteria are the “first line” of contact with nZVI. The impact of nZVI exposure cannot be generalized, because it is strongly influenced by the bacterial strain. One of the most negative effect of nZVI exposure is the formation of reactive oxygen species (ROS), that may cause the peroxidation of membrane lipids and DNA damage (Auffan et al., 2008). For example, the reaction of *Bacillus cereus* to nZVI exposure was the accelerated entry into the sporulation phase (Fajardo et al., 2013). Several cycles of the exposure of *Pseudomonas putida* F1 to low concentration of nZVI (0.1 g.l<sup>-1</sup>) led to the rise of persistent phenotype with a higher tolerance to nZVI, and complete inhibition of cell growth was observed at 5 g.l<sup>-1</sup> of nZVI (Kotchaplaí et al., 2017). The concentration of bacterial strain *Stenotrophomonas maltophilia* decreased 4 times after 140 h exposure to nZVI Nanofer 25S in the concentration of 2 g.l<sup>-1</sup> (Horváthová et al., 2019). Several studies indicate the positive effect of nZVI – effective degradation of nitrates (Shin & Cha, 2008); the formation of H<sup>+</sup>, that can act as a biostimulant for methanogene and sulphate-reducing bacteria (Cecchin et al., 2017); or the stimulation of growth of the Gram(+) bacteria (Němeček et al., 2014). Among water and soil organisms, a negative effect on reproduction, body mass and mortality were noted at earthworms *Eisenia fetida* and *Lumbricillus rubellus* already at concentrations above 100 mg soil kg<sup>-1</sup> (El-Temsah & Joner, 2012). The same research team

examined a collembola *Folsomia candida* and ostracods *Heterocrypsis incongruens* incubated with 1 or 10 g nZVI kg<sup>-1</sup> and observed severe toxic effects short time (7 days) after addition of nZVI, with a high mortality of adults. After 30 days, adults could survive in treated soils, while no juveniles were produced. The adverse effects of nZVI on test organisms seem temporary and reduces after oxidation of nZVI particles (El-Temsah & Joner, 2013). Yang et al. (2016) shows no significant mortality after 24 h exposure of the nematode *Caenorhabditis elegans* to environmentally significant concentration of nZVI coated with CMC, but the reproductive toxicity assays revealed that CMC-nZVI decreased offsprings in parental generation and increased the concentration of ROS. The reproductive toxicity was transferable from the F0 (parental) to F1 and F2 generations, but recovered in the F3 and F4 generations after parental exposure. The mammalian cells are the least examined group. The nZVI particles are able to overcome biological barriers and migrate through the body by absorption by the alveolus, small intestine or skin up to tissues and provoke the oxidative stress (Keane et al., 2009). Recently, the application of nZVI has been one of the commonly used environmental technologies. It is necessary to find a balance between the beneficiary effect of nanoremediation and potential toxicity of nZVI introduced into the environment.

This paper is focused on the nanodegradation of chlorinated ethenes using the synthetic nZVI dispersion Nanofer 25S (NANO IRON, s.r.o., CZ) from the native groundwater samples with CAH contamination from model locality: a) nanodegradation of CAH from the contaminated groundwater; b) nanodegradation of CAHs in the contaminated groundwater in the simulated geological environment representing real conditions of model locality. The main goal of the experiments was to define the effective concentrations of nZVI in the removal of CAH from saturation geological zone to the given hygienic limits (Indication (ID) and intervention (IT) criteria according to Directive of Ministry of Environment of the Slovak Republic No. 1-2015/7). Obtained experimental data will be used for the purposes of designing a real application of nanoremediation at the model locality of environmental burden.

### Characterization of investigated problem

The contaminated groundwater has been sampled from model locality in the central part of Bratislava. The area of interest is situated in the wide center of Bratislava and is a part of a large environmental load classified as confirmed environmental burden (registered as “B1 (002) / Bratislava – Old Town – Apollo – wider area of the former refinery” in the Register of environmental burdens). In the past, the

area of interest belonged to the industrial zone of the city with industrial production facilities, which significantly affected the current environmental condition of the area. The area has been used industrially since 1896, when the former Apollo oil refinery was opened. The recent pollution represented by the free phase of petroleum hydrocarbons on the groundwater surface most likely comes from a historical accident after the bombing of the Apollo refinery during the Second World War (in 1944). Pollution of groundwater and geological environment was also increased by production facilities such as Kablo, Gumon, Heating plant ZSE and Chemika. Significant extensive pollution of the rock environment and groundwater has been confirmed by several geological surveys (e.g. Janták and Polák, 2001; Auxt et al., 2002; Maloveský et al., 2006; Jantáková et al., 2018). Important contaminants such as non-polar extractable substances,  $C_{10}$ – $C_{40}$ , BTEX, PAHs and CAHs exceeded the ID and IT criteria several times (Directive of Ministry of environment of SR No. 1/2015-7) in the rock environment and groundwater. Nowadays, the industrial objects are mostly demolished and there is an intensive development of polyfunctional buildings and several remediation projects in the area of interest.

In the depths relevant from the point of view of potential remediation works, the geological environment is formed by rocks of Quaternary cover formations (Pleistocene to Holocene facies of Quaternary fluvial and anthropogenic sediments). Neogene sediments are found in their subsoil. The area of floodplain valley is mostly flat with altitude differences lower than 2 m and minimal slope of natural relief, which is formed by the Danube river – the dominant natural factor of area. The surface of area is formed by Neogene and Quaternary sediments and artificially settled with the anthropogenic layer (up to 5.1 m). The Quaternary formation is formed by 0.7–1.8 m thick positions of various anthropogenic sediments, and positions up to 4.0 m are present in some part of the model area (Janták & Polák, 2001). Below this layer are located original and compact sandy soils of the Quaternary alluvial complex. These are the youngest and most widespread fluvial sediments, rising in form of bottom lands of creeks and rivers (Pristaš et al., 1992). The thickness of this layer varies widely and in some areas is completely missing. Then the anthropogenic layer is in direct contact with the gravel layer. It is up to 12 m thick, with pebbles of  $\varnothing$  1–5 cm, in the lower parts  $\varnothing$  15–30 cm. Neogene is formed by 10.6–15.9 m thick clayey – sandy complex with pitches of gravels (Vlasko et al., 2015).

## Methodology

### *Contaminated water sampling*

Contaminated groundwater has been pumped from the hydrogeological well in central part of studied area

according to appropriate standards and technical norms into the storage container (50 l), avoiding its contact with air. Groundwater sample to determine the concentration of contaminants has been withdrawn and pH,  $E_c$  (conductivity),  $E_h$  (redox potential) values have been determined *in situ* immediately after pumping. To simulate the geological profile of the locality of environmental load, native geological substrates from drilling cores were collected. A fine gravel (fraction 4–8 mm) from the saturated zone without contamination served as the native solid samples for filling the experimental containers.

### *Characterization of the nZVI dispersion Nanofer 25S*

The degradation of CAHs was performed by aqueous dispersion Nanofer 25S (NANO IRON, Ltd., CZ) stabilized with biodegradable organic and inorganic modifiers. The iron content: 14–18 % w/w, with the particle size > 50 nm and the specific surface > 25 m<sup>2</sup>g<sup>-1</sup>. More information available at [www.nanoiron.cz](http://www.nanoiron.cz).

### *Decontamination of the groundwater with Nanofer 25S nanoparticles*

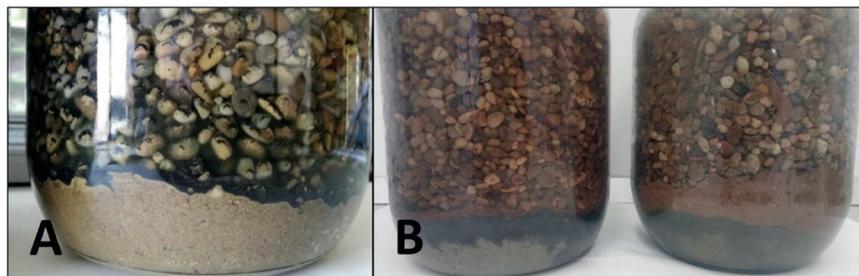
Static experiment of CAHs nanodegradation processed in 2 l glass containers closed with a joint cap with 2 l of contaminated water from the storage container. Dispersion of nZVI Nanofer 25S in the concentration 0, 1, 2, and 4 g.l<sup>-1</sup> has been added. Water samples for determining of CAHs degradation have been withdrawn after 1, 3, 7, 14, 28, and 62 days.

### *Decontamination of the groundwater in the simulated geological environment using Nanofer 25S nanoparticles*

The 5 l glass containers have been filled with inert, non-contaminated gravel with fraction 4–8 mm, representing the gravel collector of groundwater (Fig. 1). The gravel was drenched with approx. 2.5 l of contaminated water and the Nanofer 25S dispersion has been added in the same concentrations as above: 0, 1, 2 and 4 g.l<sup>-1</sup>. Each container had two drain valves for H<sub>2</sub> release and water sampling. Water samples to determine of CAHs degradation have been withdrawn after 1, 3, 7, 14, and 28 days.

While sampling, the pH,  $E_c$ ,  $E_h$  and temperature were measured in the same time intervals. pH was measured by METTLER TOLEDO Seven Compact (USA);  $E_c$  and  $E_h$  by AQUAREAD Water Monitoring Instruments (UK). Containers were mixed regularly and stored in the dark place. Water samples were immediately delivered to the laboratories. A chemical analyses of water samples were conducted in the accredited laboratories ALS Czech Republic (Praha, Czech Republic) by the gas chromatography with FID and ECD detector (method

W-VOCFID01 – CZ\_SOP\_D06\_03\_156 except chap. 9.3 (US EPA 601, US EPA 8260, US EPA 8015, RBCA Petroleum Hydrocarbon Methods) and were tested to the following CAHs: VC, *trans*-1,2-DCE, 1,1-DCE, *cis*-1,2-DCE, TCE, PCE and the sum of five chlorinated hydrocarbons.



**Fig. 1.** Experimental setup: Container with contaminated groundwater in simulated geological environment with nZVI. A – closeup of non-contaminated gravel applied as a geological environment after nZVI application. B – closeup of model geological environment after 62 days of nZVI application.

### Obtained new data and discussion

Degradation of CAHs using nZVI Nanofer 25S was carried out in the real contaminated groundwater, pumped out from the area of environmental burden and in the same contaminated water with the simulated geological environment – gravel in fraction 4–8 mm. Analysis of the CAHs concentration showed that VC, *trans*-1,2-DCE and 1,1-DCE were measured at insignificant concentrations already at the input (immediately after pumping from the well) (Tab. 1), therefore their degradation was not evaluated.

### Decontamination of the groundwater with Nanofer 25S nanoparticles

Fig. 2 summarizes the nanodegradation of CAHs in the contaminated groundwater with Nanofer 25S dispersion at various concentrations (1, 2 and 4 g.l<sup>-1</sup>). A bottle without the addition of nZVI served as the control of nZVI effectivity and the figure shows that the degradation of selected hydrocarbons (*cis*-1,2-DCE, TCE and PCE) runs even without the nZVI addition (Fig. 2 A). In a closed environment, PCE was degraded spontaneously in the same extent as with the nZVI particles. Various concentrations of nZVI had no effect on the degradation of CAHs, only minimal differences were observed. After 62 days of degradation, almost 100 % of 1,2-DCE, TCE, PCE and a sum of 5 CAHs was removed from the contaminated groundwater.

### Decontamination of the groundwater in the simulated geological environment using Nanofer 25S nanoparticles

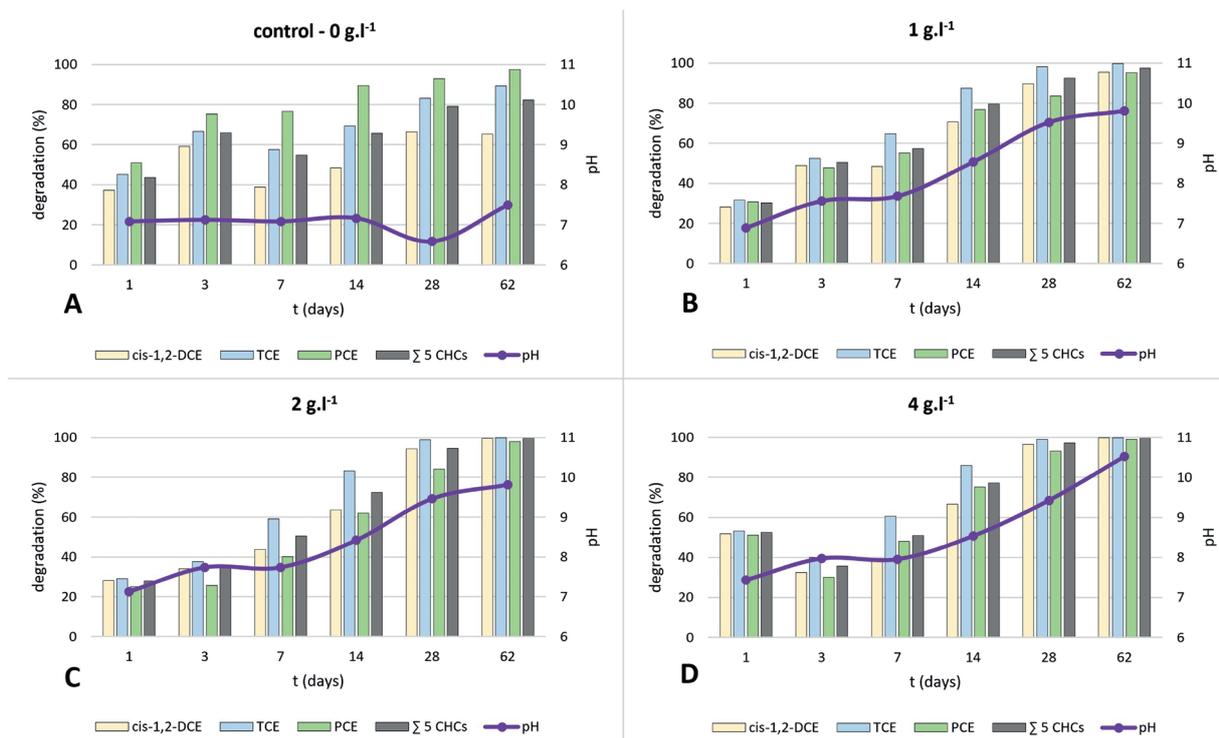
To approach the real conditions of the contaminated area, nanodegradation of CAHs was provided in the simulated geological environment represented with inert non-contaminated gravel. Results are summarized in Fig. 3. Obviously, degradation of all determined CAHs runs faster in the comparison of CAHs nanodegradation without gravel. Rock environment has a natural capability to

**Tab. 1**

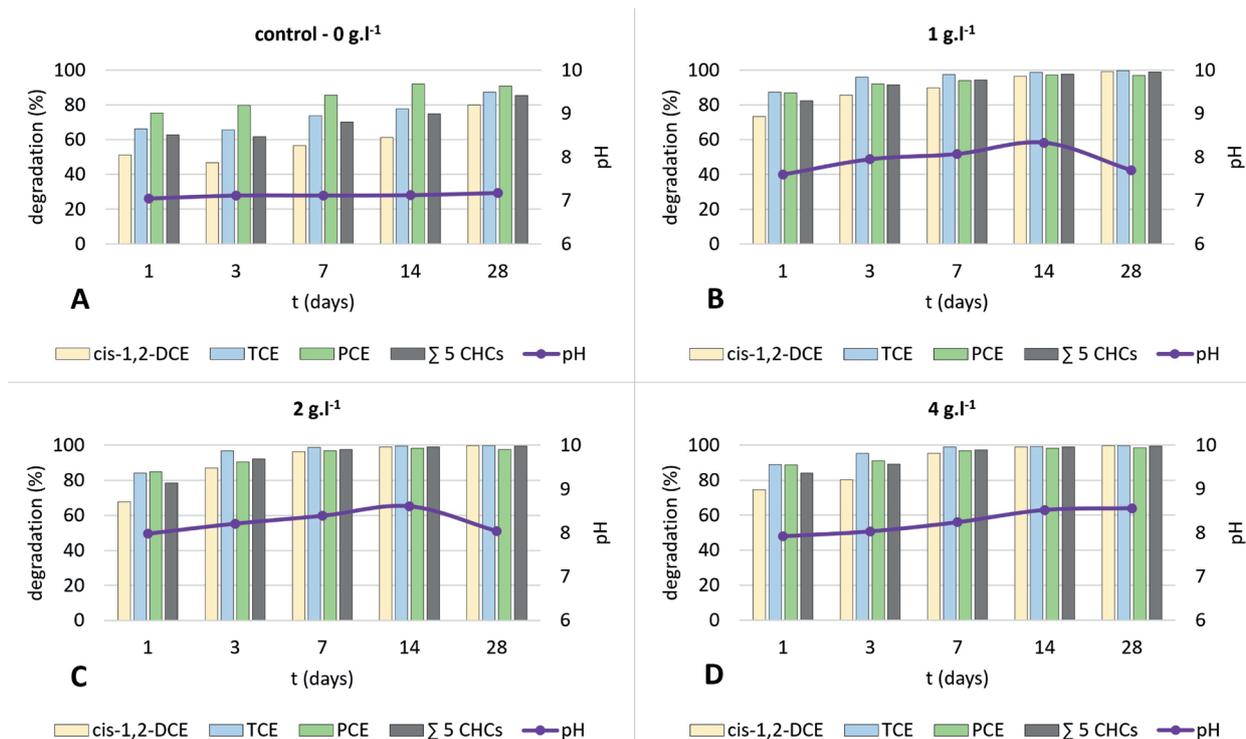
Concentrations of CAHs at the input – immediately after pumping from the well and concentrations after application of nZVI in amount 1 g.l<sup>-1</sup> to the contaminated water (A) and contaminated water in simulated geological environment (B) after 1 and 62/28 days of nanodegradation.

Contaminant	Limit of determination [µg.l <sup>-1</sup> ]	Concentration at the input [µg.l <sup>-1</sup> ]	Hygienic limits for water* [µg.l <sup>-1</sup> ]		A. Concentration in the contaminated water [µg.l <sup>-1</sup> ]	B. Concentration in the contaminated water in the simulated geological environment [µg.l <sup>-1</sup> ]
			ID	IT	62 days of nanodegradation	28 days of nanodegradation
Σ 5 CAHs	5.0	854	n/a	n/a	22	8.5
PCE	1.0	156	10	20	7.3	4.8
TCE	1.0	396	25	50	1.2	1.3
<i>cis</i> -1,2-DCE	1.0	299	25	50	13.5	2.4
1,1-DCE	1.0	1.1	10	20	< 1.0	< 1.0
<i>trans</i> -1,2-DCE	1.0	1.0	25	50	< 1.0	< 1.0
VC	4.0	< 4.0	10	20	< 4.0	< 4.0

ID – indication criteria, IT – intervention criteria according to Directive of Ministry of Environment of the Slovak Republic No. 1/2015 – 7 for the elaboration of risk assessment analysis of contaminated sites.



**Fig. 2.** Degradation of *cis*-1,2-DCE, TCE, PCE, sum of 5 CHCs from the contaminated groundwater by nanoparticles Nanofer 25S in concentration 0 – control (A), 1 (B), 2 (C), 4 g.l<sup>-1</sup> (D), and the pH course. Sampling of water for pH, E<sub>c</sub>, and E<sub>h</sub> after 1, 3, 7, 14, 28, and 62 days of static degradation.



**Fig. 3.** Degradation of *cis*-1,2-DCE, TCE, PCE, and sum of 5 CHCs from the contaminated groundwater in the simulated geological environment (non-contaminated gravel, fraction 4–8 mm) by nanoparticles Nanofer 25S in concentration 0 – control (A), 1 (B), 2 (C), and 4 g.l<sup>-1</sup> (D), and the pH course. Sampling of water for pH, E<sub>c</sub>, and E<sub>h</sub> after 1, 3, 7, 14, and 28 days of static degradation.

degrade and eliminate chlorinated compounds, especially due to the iron content.

Furthermore, carbonates of the gravel buffer the pH fluctuations caused by the addition of nZVI and release of OH<sup>-</sup> anions. In the bottles without gravel, pH value was slightly rising up from neutral to basic values after the nZVI addition (Fig. 2, Tab. 2), while in the presence of gravel, pH value remained slightly basic (7.6–8.3) throughout the nanodegradation. That could indicate the potential success of future *in situ* groundwater nanoremediation in the real geological environment. The “buffering” capacity of geological environment may attenuate the change of pH that can be responsible for undesired changes in the environmental balance (e.g. metal leaching). The temperature was increasing slightly from 20 °C to 26 °C, which designate this environment as favorable for the autochthonous bacteria with the biodegradation capabilities. Redox potential ( $E_h$ ) has a significant impact to the natural attenuation; bioavailability and toxicity of chemical substances correlate with oxidative and reductive reactions in the matrix. The groundwater without nZVI had positive  $E_h$  values, but the addition of nZVI caused the decrease to negative values, indicating the creation of reductive conditions. As mentioned above, reductive conditions are favorable for the degradation of highly chlorinated CAHs – PCE, TCE, which has been confirmed by the degradation results.

The addition of nZVI brought about the decreasing of conductivity ( $E_c$ ) values in both environments after addition of nZVI. The conductivity of the non-treated groundwater remained almost at the same level; the nZVI in the concentration of 1 g.l<sup>-1</sup> did not cause a change in conductivity immediately after addition, but during the experiment, the values were slightly decreasing. The conductivity change may be related with the pH change; alkaline environment can cause a precipitation of electrolytes in the experimental container (Waclawek et al., 2015). The crucial finding is, both approaches decreased the concentration of *cis*-1,2-DCE, TCE and PCE below the hygienic limits – ID and IT criteria (Tab. 1) for water according to the above-mentioned Directive of Ministry of Environment.

## Conclusion

It was confirmed that degradation of the groundwater CAHs in the isolated environment occurs even without the application of remediation techniques. However, spontaneous degradation in the real contaminated water is determined with the inflow of the native water. Injection of nZVI accelerated the CAH degradation, especially in the contaminated groundwater in the simulated geological environment. Almost complete degradation of *cis*-1,2-DCE, TCE, PCE and the sum of 5 CAHs were achieved, independent of the dose of nZVI (1 vs 4 g.l<sup>-1</sup>). Taking into

Tab. 2

Physical parameters ( $t$ ,  $E_h$ , pH and  $E_c$ ) measured during the nanodegradation of CAHs in the contaminated water (A) and in the contaminated water with simulated geological environment (B).

A. Contaminated water									
without nZVI, $c_{nZVI} = 0 \text{ g.l}^{-1}$					$c_{nZVI} = 1 \text{ g.l}^{-1}$				
Day	$t$ [°C]	$E_h$ [mV]	pH	$E_c$ [ $\mu\text{S.cm}^{-1}$ ]	day	$t$ [°C]	$E_h$ [mV]	pH	$E_c$ [ $\mu\text{S.cm}^{-1}$ ]
1	20.8	230.1	7.08	1 066	1	20.8	-147.1	6.89	1 046
3	22.5	140.0	7.12	930	3	23.3	-76.2	7.56	973
7	21.3	78.4	7.08	927	7	20.9	-155.8	7.68	876
14	23.5	78.8	7.16	975	14	23.5	-18.1	8.53	782
28	22.8	101.6	6.58	1 062	18	21.5	-201.7	9.52	725
62	26.3	272.6	7.49	1 017	62	25.8	-337.0	9.81	618
B. Contaminated water in the simulated geological environment									
without nZVI, $c_{nZVI} = 0 \text{ g.l}^{-1}$					$c_{nZVI} = 1 \text{ g.l}^{-1}$				
Day	$t$ [°C]	$E_h$ [mV]	pH	$E_c$ [ $\mu\text{S.cm}^{-1}$ ]	day	$t$ [°C]	$E_h$ [mV]	pH	$E_c$ [ $\mu\text{S.cm}^{-1}$ ]
1	20.7	83.1	7.04	1 022	1	21.1	-365.1	7.60	950
3	22.3	132	7.11	1 023	3	22.4	-387.0	7.95	843
7	24.6	54.2	7.11	935	7	22.1	-316.2	8.07	769
14	25.6	56.8	7.12	890	14	24.1	-253.2	8.33	692
28	22.7	106.2	7.17	1 024	28	21.8	-217.9	7.70	674

account the economic aspect, the concentration of nZVI 1 g.l<sup>-1</sup> is considered as sufficient for nanodegradation. In addition, no VC was determined, therefore it is assumed that the degradation pathway led to the formation of non-toxic products. The gravel, representing the geological environment, attenuated the alkalization of the groundwater after the nZVI addition, creating the suitable conditions for microbes with degradation abilities. Results show a potential for successful *in situ* application of nZVI, possibly in combination with other remediation approaches, which may be the definitive solution for the cleanup of polluted sites.

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## Nanodegradácia chlórovaných uhl'ovodíkov z podzemnej vody v natívnom geologickom prostredí (laboratórny vsádzkový experiment)

Degradácia chlórovaných uhl'ovodíkov (CIU) aplikáciou nanočastíc železa s nulovým mocenstvom (nZVI) do geologického prostredia predstavuje inovatívnu remediáciu metódu. Úspech takejto remediácie CIU *in situ* je podmienený realizáciou experimentov v podmienkach, ktoré čo naj dôvernejšie simulujú reálne geologické prostredie. Jednými z najnebezpečnejších a zároveň najčastejšie sa vyskytujúcich chlórovaných uhl'ovodíkov sú chlórované etény – vinylchlorid (VCM), 1,1-dichlórétén (1,1-DCE), *cis*-1,2-dichlórétén (*cis*-1,2-DCE), *trans*-1,2-dichlórétén (*trans*-1,2-DCE), trichlórétén (TCE) a tetrachlórétén (perchlórétén, PCE). V minulosti sa potenciálnej toxicite CIU nevenovala pozornosť, no v súčasnosti je známe,

že izoméry DCE a PCE sú organizáciou US EPA klasifikované ako pravdepodobné karcinogény a VCM a TCE ako potvrdené karcinogény. Cieľom tohto výskumu bola degradácia chlórovaných uhl'ovodíkov z natívnej vzorky kontaminovanej podzemnej vody v simulovanom geologickom prostredí aplikáciou disperzie nZVI Nanofer 25S. Nanočastice ako silné redukčné činidlo CIU sa degradujú mechanizmom sekvenčnej hydrogenolýzy alebo za určitých podmienok v prípade CIU s vicinálnymi chlórými substitúciami redukčnou  $\beta$ -elimináciou. CIU podliehajú nasledujúcemu rozkladu: PCE  $\rightarrow$  TCE  $\rightarrow$  DCE  $\rightarrow$  VCM  $\rightarrow$  etén. Výsledkom redukcie je teda zníženie stupňa chlórácie.

Natívna kontaminovaná voda pochádza z lokality Klingerka, nachádzajúcej sa v širšom centre Bratislavy. Podzemná voda je kontaminovaná ropnými uhl'ovodíkmi z čias bombardovania rafinérie Apollo. Voda bola odobraná jednorazovo z vrtu CS-21 čerpadlom podľa príslušných noriem a technických noriem STN.

Stacionárny experiment degradácie CIU v natívnej vode (A) prebiehal v sklenených nádobách (2 l) s natívnou kontaminovanou vodou zo zásobnej nádrže (2 l). Do fliaš bola pridaná disperzia nZVI Nanofer 25S v koncentracii 1, 2 a 4 g · l<sup>-1</sup>. Jedna nádoba ostala bez prídavku nZVI (kontrola). Stacionárny experiment degradácie CIU vo vode v simulovanom geologickom prostredí (B) sa realizoval s použitím inertného nekontaminovaného štrku s frakciou 4 – 8 mm. Takýto systém reprezentoval štrkový kolektor podzemnej vody. Test prebiehal v sklenených nádobách (5 l) naplnených štrkom a doplnených natívnou vodou zo zásobnej nádrže (ca 1,5 l). Do nádob bola pridaná disperzia nZVI Nanofer 25S v koncentracii 1, 2 a 4 g · l<sup>-1</sup>. Jedna nádoba ostala bez prídavku nZVI (kontrola). Experimenty prebiehali pri teplote 20 – 25 °C. Z nádob sa po 1, 3, 7, 14 a 28 dňoch [z nádob s natívnou vodou (experiment A) aj po 62 dňoch] odoberali vzorky a zmerali sa základné fyzikálne veličiny (t, pH, E<sub>h</sub>, E<sub>c</sub>). Koncentrácia 5 CIU (VCM, 1,1-DCE, *trans*-1,2-DCE a *cis*-1,2-DCE, TCE, PCE) a jej sumy v odobraných vzorkách sa stanovila v akreditovaných laboratóriách ALS Česká republika.

V kontaminovanej natívnej vode (experiment A) aj vo vode v simulovanom horninovom prostredí (experiment B) sa bez prídavku nZVI v priebehu trvania experimentu (62/28 dní) degradovalo vyše 80 % sumy 5 CIU. Degradácia CIU v uzavretom priestore (sklenená nádoba) prebieha do značnej miery aj samovoľne. Za túto degradáciu okrem bežných fyzikálno-chemických javov môžu byť zodpovedné aj mikroorganizmy prítomné v natívnej vode (Schiefler et al., 2018). Tie sa pri vyššej teplote (20 – 25 °C) mohli podieľať na úbytku CIU ich biodegradáciou. Realizovanými experimentmi sa

potvrdila aj účinnosť aplikácie nZVI, prídavkom disperzie Nanofer 25S sa v oboch systémoch za rovnaký čas (62/28 dní) dosiahla kompletná, 100 % degradácia sumy 5 CIU. Sledovali sa len minimálne rozdiely v degradácii pri rôznej koncentrácii nZVI, takže na degradáciu CIU v uzavretom prostredí postačuje disperzia nZVI v koncentrácii 1 g · l<sup>-1</sup>.

V simulovanom horninovom prostredí vytvorenom prídavkom inertného štrku prebiehala degradácia rýchlejšie – v nádobách s nZVI aj v kontrole. Už po 7 dňoch pôsobenia nZVI sa degradácia približovala k 100 %, no v nádobách bez štrku sa za rovnaký čas sledovala degradácia nižšia takmer o 40 %. Horninové prostredie má prirodzenú schopnosť odbúravať a eliminovať chl'ované uhl'ovodíky najmä vďaka prítomnosti železa. Prítomnosť karbonátov horninového prostredia zároveň tlmí výkyvy pH spôsobené prídavkom nZVI. V nádobách bez štrku sa pH po prídavku nZVI zvyšovalo, v prítomnosti štrku sa hodnota pH držala v neutrálnej, resp. jemne bázičkej oblasti. Takéto prostredie je potenciálne vhodné aj pre autochtónne mikroorganizmy s biodegradáčnymi schopnosťami.

Sanácia vodného, resp. horninového prostredia nanoželezom patrí medzi inovatívne sanačné technológie a je možné ju efektívne kombinovať s rôznymi biologickými prístupmi či fyzikálno-chemickými postupmi, napr. podporou elektrickým prúdom a pod. Potvrdilo sa, že proces degradácie CIU prebieha aj bez aplikácie akýchkoľvek sanačných techník, no v reálnom prostredí by bola samovoľná degradácia determinovaná prítokom čerstvej natívnej vody. Injektáž nZVI vo vhodne zvolenej koncentrácii do podzemnej kontaminovanej vody by v takomto prípade mohla proces degradácie urýchliť a zefektívniť. V uzavretom prostredí sa v natívnej vode aj vo vode v simulovanom geologickom prostredí dosiahla kompletná degradácia sumy 5 chl'ovaných uhl'ovodíkov.

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