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USE OF VARIOUS ZERO VALENT IRONS FOR DEGRADATION OF CHLORINATED ETHENES AND ETHANES

WYKORZYSTANIE RÓŻNYCH RODZAJÓW ZEROWARTOŚCIOWEGO ŻELAZA W CELU DEGRADACJI CHLOROWANYCH ETENÓW I ETANÓW

Abstract: Amongst all of the reducing agents that can be used in environmental remediation, zero valent iron (ZVI) is one of the most common due to its environmental acceptance, high reaction rate, good availability, and long-term stability. Moreover, ZVI mobility, stability and reactivity can be enhanced by the application of a DC electric current, *ie* electrokinetics (EK). In the study, six various slurries containing different ZVI were tested for their efficacy for chlorinated ethenes and ethanes degradation. Chlorinated compound concentrations, pH, oxidation-reduction potential (ORP) and conductivity were determined during the long-term kinetic test. Kinetic rate constants calculated for the degradation of three chlorinated ethenes (PCE, TCE and cis-DCE) concluded that EK brings substantial contribution to chlorinated compounds degradation. Nano-scale zero valent iron STAR had the highest reaction rates compare to the other ZVI tested. The performed study could serve as a preliminary assessment of various available ZVI before in-situ application.

Keywords: zero valent iron, nano zero valent iron, electro-activation, chlorinated aliphatics, remediation

Introduction

Iron is one of the most ubiquitous elements in the earth's crust. The use of zero valent iron (ZVI) for subsurface remediation of sites contaminated with chlorinated compounds and heavy metals has received significant attention in part due to the ability of ZVI to rapidly transform contaminants in controlled laboratory experiments. ZVI is a reactive metal with a standard oxidation-reduction potential (–0.44 V) [1]. The contamination removal mechanism by ZVI concerns the directional transfer of electrons from Fe^0 to the contaminant, which can convert the latter into non-toxic or less toxic forms [2].

ZVI has been used for the dehalogenation of various organic [3-6] and inorganic [7, 8] compounds. Field-scale applications of granular ZVI have been performed successfully since the mid-1990s and were mostly constructed as funnel-and-gate systems [7]. Another

way of applying ZVI in-situ is by permeable reactive barriers (PRBs), which have received a great deal of attention since they were proposed by Gillham and O'Hannesin [9] and have been used in-situ for a broad range of contaminants including chlorinated aliphatics and other volatile organic compounds (VOCs) [9, 10].

Chlorinated aliphatics were intensively used in the past *inter alia* in dry cleaning, in the production of decaffeinated coffee or as anaesthetic gases in hospitals. Therefore, after discovering their toxic properties, they became one of the most common contaminations of concern (CoC). Gillham and O'Hannesin [9] were the first to show the capability of ZVI for the dehalogenation of chlorinated ethanes and methane. Not much later, Matheson and Tratnyek [11] reported fast dehalogenation of trichloroethene (TCE) and CCl_4 using ZVI.
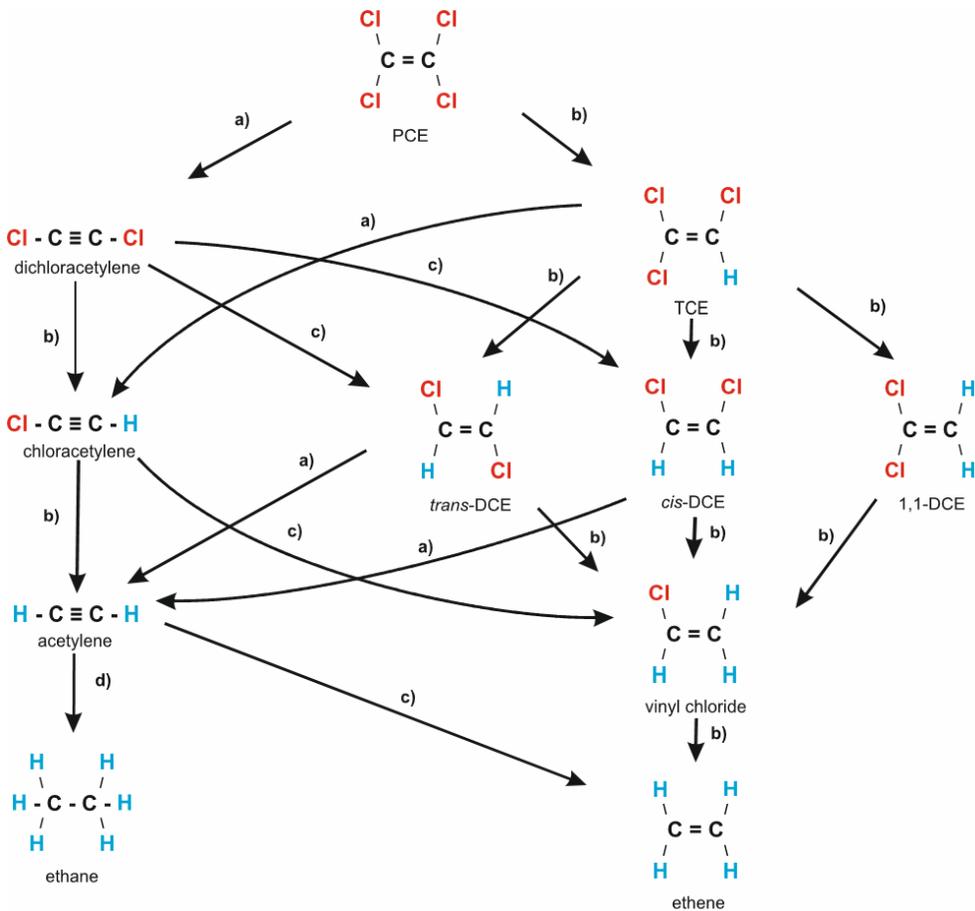

Fig. 1. Proposed reduction pathway of chlorinated ethenes: a) reductive dehalogenation, b) hydrogenation, c) reduction of acetylene to ethene, d) reduction of acetylene to ethane

Arnold and Roberts [12] described the reduction mechanism of chlorinated aliphatics by ZVI and concluded that the reduction takes place mainly by α- or β-elimination.

The observed products of perchloroethene (PCE) and TCE reduction include cis-1,2-dichloroethene (cis-1,2-DCE) and vinyl chloride (Fig. 1) [2]. These compounds are regulated as contaminants in drinking water. Moreover, lesser chlorinated ethenes (especially cis-1,2-DCE) can also occur in "weathered" plumes [2]. More importantly, the highly toxic and inherent in bacteria anaerobic dehalogenation pathway - vinyl chloride, can often be circumvented within the ZVI reaction with VOCs [12].

Many studies have reported superior contaminant degradation rates by nano-sized zero valent iron (nZVI) in contrast to bulk iron particles [7, 13]. However, nZVI tends to agglomerate into large structures due to its high surface energy, which makes it difficult to be separated and recovered after use [14]. Also, the high reactivity of nZVI can become a double-edged sword preventing nZVI from reaching the contamination zone or raising competition for surface active sites between contaminants and compounds other than CoC (*eg* natural organic matter) [15]. To maintain the stability and reactivity of nZVI, numerous researchers focused on the optimal synthesis conditions of nZVI or its surface modifications. Many techniques like the addition of an iron oxide shell (nZVI Star) [16] or polymer stabilization (carboxymethylcellulose (CMC)/nZVI) [17] can be applied, enhancing the dispersion of nZVI and efficiently sustaining their reactivity. Stabilisation with gums [18], smectite [19], and poly(methylmethacrylate) [20] can also be employed to stabilize the nZVI for remediation of CoC. These stabilizations are accomplished by boosting the steric or electrostatic repulsions between the particles to inhibit nZVI aggregation. At the same time, the degradation effectiveness of CoC by surface modified nZVI can significantly increase in comparison to conventional nZVI [18]. A further action that can be used to prolong ZVI mobility and stability [18] and reactivity with CoC [21-23] is application of a DC current, *ie* electrokinetics (EK).

Yi-Chu Huang [21] investigated the performance of permeable reactive barriers packed with nZVI particles enhanced by a surfactant and EK on TCE degradation. Chlorinated byproducts were not detected during lab-scale sandbox tests, and TCE was completely dechlorinated. The results of these tests showed that EK can promote the reactivity of nZVI by releasing H+ near to the anode. Protons not only participate in the TCE dechlorination reaction but also wash away the precipitates on the surface of the nZVI to maintain its activity. On the other hand, Fan et al [18] created a novel technology called EK + gum stabilized nZVI/Pd and used it to remediate soil contaminated with polychlorinated biphenyls (PCBs). Xanthan gum was used to stabilize nZVI/Pd. The stabilised nanoparticles were successfully transported along with the soil column by EK, and an apparent increase of Fe content was found towards the cathode. Moreover, they determined that a higher electroosmotic flow favoured the migration of nanoparticles.

Purpose of this work was to study effectiveness of various ZVI and influence of electrokinetics in dehalogenation of chlorinated ethenes and ethanes. Due to a high cost of nZVI in the environmental applications, a combination (w/w) of nZVI with much cheaper μZVI was tested as well.

Methodology

Materials

Micro-scale zerovalent iron (mZVI) was purchased from Shrutarth Chemicals, (Gujarat, India). Nano-scale ZVI (Nanofer Star, Fe^0 stabilized with a thin iron oxide shell

and Nanofer N25S, Fe^0 modified with a combination of a biodegradable organic and inorganic stabilizer) [24] were provided by NANO IRON, s.r.o. (Czech Republic).

Contaminated groundwater was taken from the Pisecna site (Czech Republic). The Pisecna site is an old environmental liability that originated at the site of a former landfill of OEZ Letohrad (Czech Republic). The water from the site was taken from 10 meters below the ground surface, collected in a 20 litre cylinders, transferred to the laboratory, and stored at 4°C under anoxic conditions. The contaminant composition was determined prior to the experiments and is shown in Table 1.

Table 1

Composition of contaminated groundwater from the Pisecna site

CoC	Concentration [µg/dm³]
1,1,2-Trichlorethane	139
1,1-Dichloroethene	55
1,2-Dichlorethane	3,643
cis-1,2-Dichloroethene (cis-1,2-DCE)	378
Perchloroethene (PCE)	18,530
Trichloroethene (TCE)	13,040

Analytical

CoC were qualitatively searched for in the full scan mode of a GC/ion trap MS instrument (Varian Saturn 3800), equipped with a VF-624ms column, 60 m in length, 0.32 mm in diameter and 1.8 µm in film thickness. Helium was used as a carrier gas with a flow rate of 1 cm^3/min. The pH, ORP and conductivity were measured by a WTW pH-meter equipped with SenTix pH electrodes (TMultiLine® Multi 3430 IDS). The ORP values were corrected to the standard hydrogen electrode (SHE).

Experimental design

Tests were performed in 2.5 dm^3, air-tight reactors, at a constant temperature of 23°C and stirred at a constant rate of 200 rpm. The same dose (5 g/dm^3) of various ZVIs and their combinations (Table 2) was added to the reactors.

Table 2

Composition of ZVIs used in the experiments

	nZVI used [%]	µZVI used [%]	DC current used
nZVI N25S	100	0	No
nZVI Star	100	0	No
nZVI Star + µZVI	33	67	No
nZVI Star + µZVI + DC	33	67	Yes
µZVI	0	100	No
µZVI + DC	0	100	Yes

A DC power supply (HQ POWER PS3010) was used for the electro-activation under the conditions of: 5 V and 9.5 mA. For this tests, iron electrodes at an inter-electrode distance of 8 cm, were used. The experimental design can be seen in Figure 2.
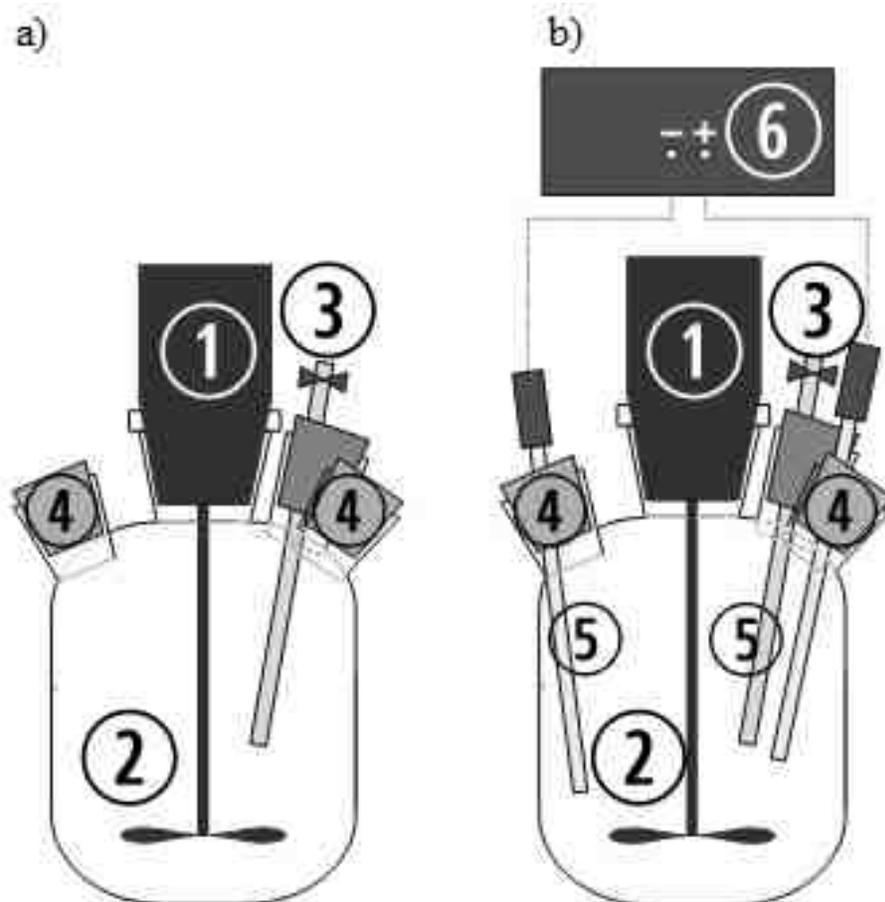
Fig. 2. Schematic diagram of the reactors: a) without electro-activation, b) with electro-activation; 1 - stirrer, 2 - glass reactor with contaminated groundwater, 3 - sampling port, 4 - rubber caps, 5 - iron electrodes, 6 - DC power supply

Results and discussion

pH, ORP and conductivity changes during the experiment

The initial pH of the groundwater was 7.6. In almost all of the reactors the pH value increased significantly (8.5-11) after the addition of ZVI (Fig. 3). The pH increase could be caused by reaction of the ZVI with the water, therefore releasing OH⁻ anions and increasing the pH (Eq. 1):

$$\text{Fe}^0_{(s)} + 2\text{H}_2\text{O}_{(l)} \rightarrow \text{Fe}^{2+} + \text{H}_{2(g)} + 2\text{OH}^-_{(aq)} \quad E^0 = -0.39 \text{ V} \tag{1}$$

After 15 days, pH started to decrease and ORP increase, which could be explained by the slow depletion of the ZVI or diminution of its reactivity.
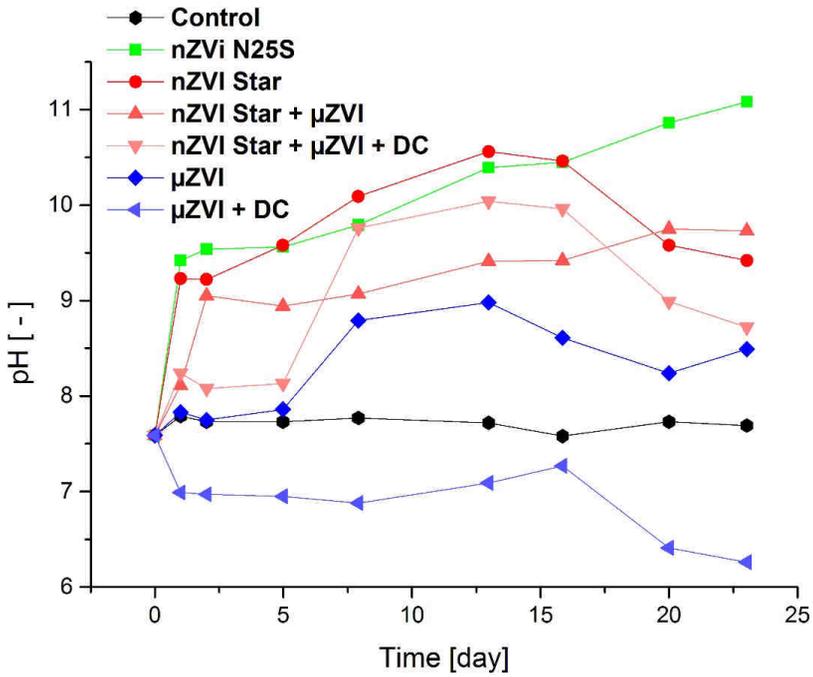
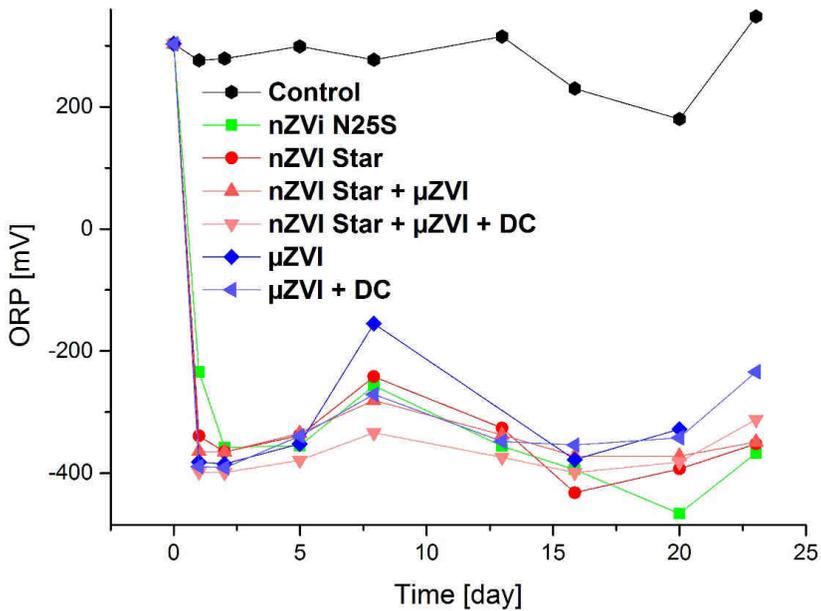Fig. 3. Changes in the pH value over time
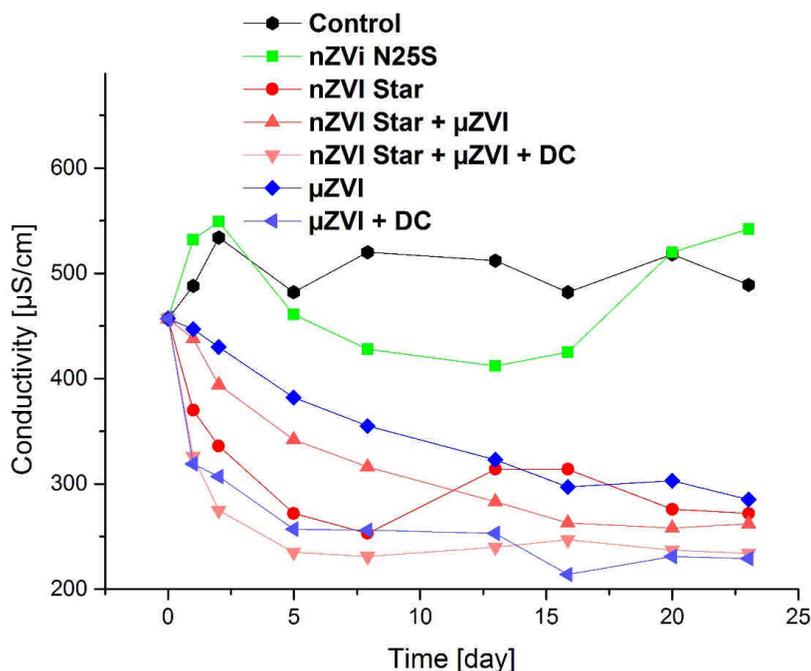

Fig. 4. Changes in ORP over time

Fig. 5. Changes in conductivity over time

The addition of an electric current (EC) in the reactors: "µZVI + DC" and "nZVI Star + µZVI + DC" resulted in a smaller pH change.

Changes in oxidation-reduction potential (ORP) and conductivity during the experiment are shown over time in Figures 4 and 5, respectively. During the tests, the ORP values decreased sharply from about 300 to –400 mV as the ZVI was added to the reactors. The measured differences between the ZVI types are small comparable to experimental error of the measurement. At the end of measured period, ORP started to increase back similarly to changes in pH.

The conductivity changes can be attributed to the pH change and precipitation of electrolytes in the reactor. During the tests, the quantity of sulphates and nitrates was monitored and a significant reduction in both was observed. Therefore, the composition of electrolytes changed, lowering the conductivity value. However, the highest conductivity decrease can be observed in the reactors with the electric current, which can be explained by an additional change in the structure of the electrolytes caused by electrolysis [25].

Degradation kinetics

Various size, stabilization and inducement methods (*eg* an electric current) can influence the apparent dehalogenation rate constants of ZVI. Because of their small size (often <100 nm) and a larger specific surface area, nZVIs have more reactive sides and higher efficiency in the removal of contaminants. Therefore, in comparison with commercial microscale iron, nZVIs reflect much higher dechlorination activity [7].
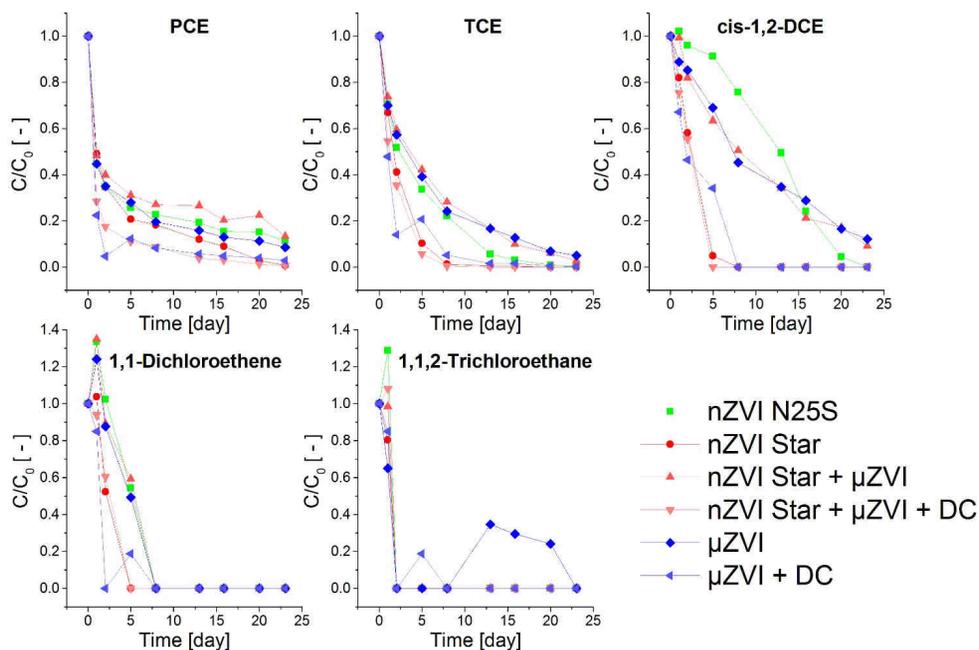
Fig. 6. Degradation of CoC by various iron types

As can be seen in Figure 6 very high reaction rates were found for the removal of chlorinated ethenes by nZVI Star, nZVI Star + µZVI + DC and µZVI + DC.

In addition, none of the presented utilization methods were successful in 1,2-Dichloroethane abatement. Highly toxic and volatile - vinyl chloride (VC) was under the detection limit (1 µg/dm^3) in almost all of the reactors. Very small VC concentrations were observed in the reactors with nZVI N25S (40 µg/dm^3) and nZVI Star + µZVI (24 µg/dm^3).

The degradation of several CoCs can fit well to the pseudo first order kinetic model:

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{2}$$

where C and C_0 are the CoC concentrations at time (t) and $t = 0$, respectively, and k is the reaction rate constant.

The calculated pseudo first order rate constants (k) can be observed in Table 3.

It can be deduced from Table 3 that a combination of nZVI Star, µZVI and DC obtained the highest decontamination rate of PCE (0.170 day^{-1}) and TCE (0.655 day^{-1}). As for cis-1,2-DCE, nZVI Star alone showed the fastest depletion rate (0.633 day^{-1}). Not surprisingly, µZVI had the smallest dehalogenation efficiency in almost all cases tested. However, coupling µZVI with the DC current could even double its degradation efficacy.

Table 3

Decontamination rate constants of selected chlorinated ethenes

	PCE		TCE		cis-1,2-DCE	
	k [day^{-1}]	R^2	k [day^{-1}]	R^2	k [day^{-1}]	R^2
nZVI N25S	0.083	0.859	0.230	0.989	0.132	0.805
nZVI Star	0.166	0.918	0.367	0.931	0.633	0.946
nZVI Star + μZVI	0.059	0.766	0.141	0.989	0.098	0.984
nZVI Star + μZVI + DC	0.170	0.950	0.655	0.991	0.294	0.999
μZVI	0.069	0.790	0.120	0,984	0.088	0.989
μZVI + DC	0.119	0.800	0.237	0.953	0.203	0.883

Conclusions

In presented study, groundwater contaminated by chlorinated ethenes and ethanes was experimentally treated by six various combinations of ZVI, namely 2 nano-sized ZVI and one micro-sized ZVI types, together with electrokinetics. Although all types of nZVI had great dehalogenation efficacy, it was not much different from the mixture containing 33% of nZVI with majority of μZVI. Furthermore, addition of the electric current (eletrokinetics) significantly increased ZVI degradation efficiency. Moreover, significance of this research is that the cost of μZVI is several fold lesser than the nZVI, therefore by the use of this mixture expenditures of in-situ applications can be significantly lowered.

Acknowledgements

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Abstrakt: Wśród wszystkich czynników redukujących, które mogą być stosowane w remediacji środowiska, zerowartościowe żelazo (ZVI) jest jednym z najbardziej popularnych ze względu na jego niedużą toksyczność, dobrą dostępność, szybkość reakcji oraz stabilność. Ponadto, mobilność, stabilność i reaktywność ZVI może być zwiększona poprzez zastosowanie prądu stałego, tzn. elektrokinetyki (EK). W przeprowadzonych badaniach przetestowano sześć rodzajów zawiesin zawierających różne typy ZVI pod kątem ich skuteczności usuwania chlorowanych etanów i etenów. W trakcie długotrwałych testów kinetycznych badano: stężenie chlorowanych węglowodorów, pH, potencjał redoks i rezystywność. Ponadto zostały policzone stałe szybkości degradacji dla trzech chlorowanych etenów (PCE, TCE i cis-DCE) i stwierdzono, że proces elektrokinetyki wspomaga zerowartościowe żelazo w obniżaniu koncentracji chlorowanych węglowodorów. Nanożelazo na zerowym stopniu utlenienia STAR okazało się najbardziej efektywne w porównaniu do innych testowanych ZVI. Przeprowadzone badania mogą posłużyć do wstępnej oceny różnych dostępnych ZVI przed zastosowaniem in-situ.

Słowa kluczowe: żelazo na zerowym stopniu utlenienia, nanożelazo na zerowym stopniu utlenienia, elektroaktywacja, chlorowane węglowodory, remediacja