Science of the Total Environment 485–486 (2014) 739–747

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Nanoscale zero-valent iron application for in situ reduction of hexavalent chromium and its effects on indigenous microorganism populations

Jan Němeček [a], Ondřej Lhotský [b], Tomáš Cajthaml [c,*]

[a] ENACON s.r.o., Krčská 16, CZ-140 00 Prague 4, Czech Republic
[b] DEKONTA a.s., Volutová 2523, CZ-158 00 Prague 5, Czech Republic
[c] Institute of Microbiology, Academy of Sciences of the Czech Republic, v.v.i., Vídeňská 1083, CZ-142 20 Prague 4, Czech Republic

HIGHLIGHTS

- The injection of nZVI in-situ resulted in a decrease of Cr(VI) in the groundwater.
- No significant changes in ecotoxicity of the groundwater have been observed.
- PLFA of soil samples showed that nZVI stimulated the growth of G+ bacteria.
- PCA showed a correlation between bacteria and iron content after the application.

ARTICLE INFO

Article history:
Received 30 June 2013
Received in revised form 4 November 2013
Accepted 22 November 2013
Available online 22 December 2013

Keywords:
Hexavalent chromium
nZVI
Toxicity
Indigenous microorganisms
Phospholipids fatty acid analysis
PLFA

ABSTRACT

Because of its high toxicity and mobility, hexavalent chromium is considered to be a high priority pollutant. This study was performed to carry out a pilot-scale in-situ remediation test in the saturated zone of a historically Cr(VI)-contaminated site using commercially available nanoscale zero-valent iron (nZVI). The site was monitored before and after the nZVI application by means of microbial cultivation tests, phospholipid fatty acid analysis (PLFA) and toxicological tests with *Vibrio fischeri*. Injection of nZVI resulted in a rapid decrease in the Cr(VI) and total Cr concentrations in the groundwater without any substantial effect on its chemical properties. The ecotoxicological test with *V. fischeri* did not indicate any negative changes in the toxicity of the groundwater following the application of nZVI and no significant changes were observed in cultivable psychrophilic bacteria densities and PLFA concentrations in the groundwater samples during the course of the remediation test. However, PLFA of soil samples revealed that the application of nZVI significantly stimulated the growth of Gram-positive bacteria. Principle component analysis (PCA) was applied to the PLFA results for the soil samples from the site in order to explain how Cr(VI) reduction and the presence of Fe influence the indigenous populations. The PCA results clearly indicated a negative correlation between the Cr concentrations and the biota before the application of nZVI and a significant positive correlation between bacteria and the concentration of Fe after the application of nZVI.

1. Introduction

Chromium is one of the most abundant heavy metals, causing pollution of groundwaters and soil due to its frequent industrial application. Chromium occurs naturally mainly in the trivalent Cr(III) and hexavalent Cr(VI) forms. The majority of its adverse effects is caused by Cr(VI) because of its solubility, mobility and high oxidizing potential leading to generally higher toxicity causing health problems such as liver damage, pulmonary congestion, vomiting and severe diarrhea (Nriagu and Nieboer, 1988). On the other hand, Cr(III) is less reactive and toxic and can be readily precipitated out of solution. Therefore, the majority of in situ treatment methods employed at the present time utilize geo-fixation of Cr(VI) by its reduction to Cr(III) and formation of insoluble Cr(III) compounds (Jardine et al., 1999). A number of articles have been published to date describing various applications of individual biological or chemical approaches to precipitate chromium into its insoluble Cr(III) form. One of the most promising methods is reduction using iron-based materials such as zero-valent iron and dissolved Fe(II) and solids containing Fe(II) (Barrera-Díaza et al., 2012).

Interest has increased over the past few years in using zero-valent iron (Fe0) and its respective nano-scale form to reduce chromium (VI) contamination (see e.g. Barrera-Díaza et al., 2012 and references therein). Zero-valent iron (ZVI) is a readily available and low-cost reducing agent that is also used extensively to remove a number of other kinds of contaminants, such as chlorinated compounds (Gomes et al., 2013), pesticides (Zhang et al., 2011) and heavy metals e.g. As(V) (Morrison et al., 2002). Although the efficiency of ZVI and especially nano-scale

* Corresponding author. Tel.: +420 241062498; fax: +420 241062384.
E-mail address: cajthaml@biomed.cas.cz (T. Cajthaml).

0048-9697/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2013.11.105

ZVI (nZVI) in reducing the concentrations of Cr(VI) and other pollutants is well documented, only a few works have focused on its ecotoxicity for indigenous organisms in the soil (Xiu et al., 2010; Fajardo et al., 2012; Pawlett et al., 2013; El-Temsah and Joner, 2012).

This study was carried out to perform a pilot-scale in-situ remediation test in the saturated zone of a historically Cr(VI)-contaminated site using commercially available nZVI. The effects of the application of nZVI on the indigenous bacteria and groundwater toxicity were also evaluated. The site was monitored before and after application of nZVI using microbial cultivation tests, phospholipid fatty acid analysis (PLFA) and toxicological tests with *Vibrio fischeri*. In particular, multidimensional statistical analysis was applied to the PLFA of soil samples from the site in order to explain how reduction of Cr(VI) and the presence of Fe affect the indigenous populations.

2. Materials and methods

2.1. Test site

The pilot test was performed at the Kortan site in Hradek nad Nisou, Czech Republic. The site is polluted with Cr(VI) originating from potassium dichromate formerly used for Cr(III) salt production for leather tanning. The process was terminated in the early 1990's. Cr(VI) concentrations in the groundwater do not currently exceed 3 mg/l. The aquifer lies in Quaternary sands and gravels with clayey admixture. The groundwater table fluctuates at a depth of 4.5–5.5 m below the surface of the ground and the aquifer has a saturated thickness of approximately 5 m. The groundwater flow velocity varies from 0.2 to 2 m/day, based on the results of well logging — a method of gradual dilution of a tracer in a well (Mares, 1977). The groundwater discharges into a local river located at a distance of 500 m. The groundwater is of the Ca-SO_4 type and is characterized by low mineralization (total dissolved solids < 0.3 g/l), rather low pH (5.4), high oxidation-reduction potential (450 to 550 mV) and low TOC (<1.5 mg/l) (Fig. 1).

2.2. Pilot application of nZVI

In order to perform the pilot test, a total amount of 120 kg of nZVI (NANOFER 25 — produced by NANO IRON, Ltd., Czech Republic) mixed with 60 m^3 of tap water (2 g/l of nZVI) was applied at the end of August 2012. The nZVI suspension was prepared at the site by dilution of 30% nZVI concentrate (provided by the vendor) using a submersible pump in 1 m^3 containers directly prior its injection. The suspension was applied to 3 different injection wells situated perpendicular to the groundwater flow. The injection wells were cased with high-density polyethylene (HDPE) casing of 80 mm ID and are screened to the whole thickness of the aquifer (5–8.3 m below the surface of the ground). The amount of nZVI applied (2 kg nZVI/ton of soil) was previously assessed by laboratory tests of reduction of Cr(VI) by nZVI using local soil and groundwater (data not shown). For this amount of nZVI,

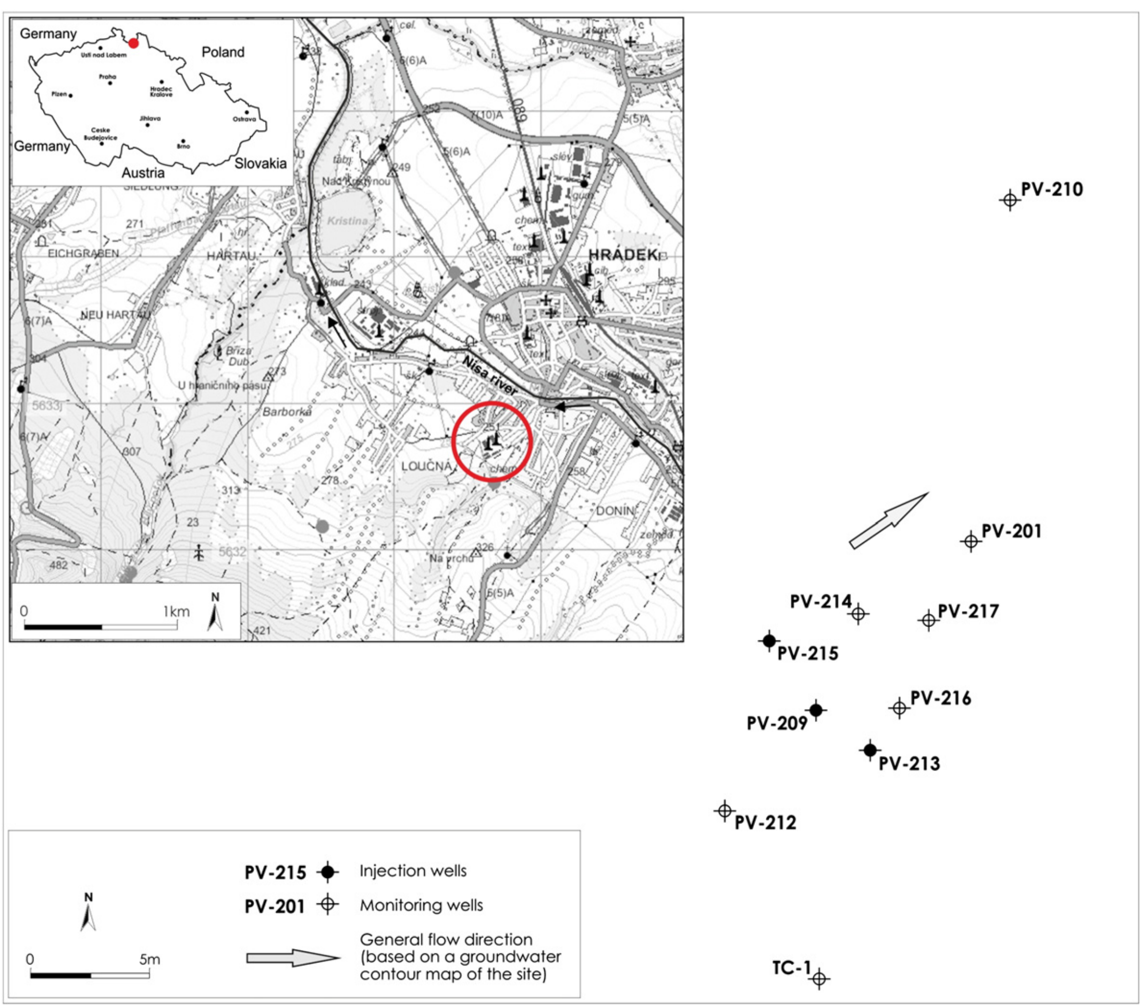

Fig. 1. Location of the contaminated site of Kortan in Hradek nad Nisou, layout of the field pilot test.