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Combined abiotic and biotic in-situ reduction of hexavalent chromium in groundwater using nZVI and whey: A remedial pilot test

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HIGHLIGHTS

- *In-situ* whey application after nZVI supported microbes to reduce efficiently Cr(VI).
- Reduction was mediated mainly by iron and sulphate reducing bacteria.
- Bacteria recovered previously spent nZVI into Fe(II).
- Recycled nZVI and natural iron in Fe(II) form enabled further Cr(VI) reduction.
- Efficient Cr(VI) removal was observed for 10 months.

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ABSTRACT

The paper describes a pilot remediation test combining two Cr(VI) geofixation methods – chemical reduction by nanoscale zero-valent iron (nZVI) and subsequent biotic reduction supported by whey. Combination of the methods exploited the advantages of both – a rapid decrease in Cr(VI) concentrations by nZVI, which prevented further spreading of the contamination and facilitated subsequent use of the cheaper biological method. Successive application of whey as an organic substrate to promote biotic reduction of Cr(VI) after application of nZVI resulted in a further and long-term decrease in the Cr(VI) contents in the groundwater. The effect of biotic reduction was observed even in a monitoring well located at a distance of 22 m from the substrate injection wells after 10 months. The results indicated a reciprocal effect of both the phases – nZVI oxidized to Fe(III) during the abiotic phase was microbially reduced back to Fe(II) and acted as a reducing agent for Cr(VI) even when the microbial density was already low due to the consumed substrate. Community analysis with pyrosequencing of the 16S rRNA genes further confirmed partial recycling of nZVI in the form of Fe(II), where the results showed that the Cr(VI) reducing process was mediated mainly by iron-reducing and sulfate-reducing bacteria.

1. Introduction

Chromium is one of the most toxic and common metal pollutants [1]. A large number of contaminated sites are related to its extensive use in industry, such as in chromium plating, production of alloys, leather tanning and wood preservation. Chromium occurs in the environment mainly as the hexavalent and trivalent species. The hexavalent form, Cr(VI), has high oxidizing potential and the species is highly mutagenic, carcinogenic and toxic [2,3]. Cr(VI) is soluble in water and thus mobile in the environment. Consequently, this pollutant can be transported to large distances from the source of the contamination. In contrast, Cr(III) is substantially less toxic and forms insoluble complexes, such as $Cr_xFe_{(1-x)}(OH)_3(s)$, $Cr_xFe_{(1-x)}OOH(s)$ or $Cr(OH)_3(s)$. Therefore, the majority of in-situ treatment methods employed at the present time utilize remediation of Cr(VI) by its reduction to Cr(III) and formation of insoluble compounds [4]. A number of articles have been

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published describing applications of various biological or chemical approaches to transform Cr(VI) into its insoluble Cr(III) form [5,6]. One of the promising chemical methods is the application of reduced forms of iron materials, mainly zero-valent iron and its nano forms (nZVI) (see Gheju and references therein) [7].

The method of biotic reduction of Cr(VI) utilizes the ability of microorganisms to enzymatically transform Cr(VI) to Cr(III). A number of aerobic as well as anaerobic microorganisms are capable of reducing Cr(VI) [5]. The aerobic bacteria utilize either soluble or membrane-associated enzymes mainly as a mechanism related to chromium resistance [8,6]. Anaerobic bacteria can use Cr(VI) as an electron acceptor in the electron transport chain related to their respiratory reactions [8].

An indirect means of anaerobic microbially mediated reduction of Cr(VI) comprises production of soluble ferrous ions (Fe(II)) or Fe(II)-bearing minerals (e.g. FeS) as a result of anaerobic oxidation of an organic substrate by iron-reducing bacteria where Fe(III) acts as an alternative electron acceptor. Cr(VI) as chromate ($CrO_4{}^{2-}$) or bichromate ($Cr_2O_7{}^{2-}$) then reacts with biogenic Fe(II) to form insoluble $Cr_xFe_{1-x}(OH)_3$ (s) or $Cr(OH)_3$(s) [9,10]. Similarly, hydrogen sulphide (H_2S) produced from microbially mediated reduction of sulfates by sulfate-reducing bacteria is able to reduce Cr(VI) to Cr(III) [11,12,9].

One of the inherent problems related to biotic reduction of Cr(VI) is that its levels in groundwater can be too toxic for autochthonous bacteria potentially utilizing Cr(VI). In our previous work, we focused on changes in the ecotoxicity of a Cr(VI) contaminated site and documented that the application of nZVI stimulated the growth of autochtonous bacteria in the aquifer soil due to significant transformation of Cr(VI) to Cr(III) [13]. However, the long-term effect of the nZVI employed was observed within a limited radius of 2 m and nZVI action was limited in more distant monitoring wells [13]. Therefore, the present study was performed to continue the pilot test at the site with application of an organic substrate to support the newly developed microbial consortium in the aquifer. Thus, the whole remediation method under study comprises chemical reduction by nZVI for treatment of the source zone with high concentrations of Cr(VI) and the biological step for remediation of the plume and/or as a further step for the pre-treated source zone. Combination of these two methods can enjoy the benefits of both of them – a rapid decrease in Cr(VI) concentrations in the groundwater by nZVI prevents further spreading the contamination and allows subsequent use of the economical biological method when residual contents of Cr(VI) are less toxic for autochthonous microorganisms directly or indirectly reducing Cr(VI). Important objectives of the study included verifying the overall feasibility and efficiency of the combined method and assessing the impact of both the abiotic and the biotic phases of the method on the biological and chemical status of the aquifer.

2. Materials and methods

2.1. Test site

The pilot test was performed in 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 1990ís. Cr(VI) concentrations in the groundwater did not exceed 3 mg L^{-1} (Fig. 1) and Cr(VI) concentrations in the aquifer soil were 2–46 mg/kg prior to the test. The aquifer is situated in Quaternary sands and gravels with clayey admixture. The groundwater table fluctuates at a depth of 4.5–5.5 m below ground level and the aquifer has a saturated thickness of approximately 5 m. The groundwater flow velocity varies from 0.2 to 2 m day^{-1}, based on the results of a tracer test (well logging) – a method of gradual dilution of a tracer in a well [14]. The groundwater is of the Ca-SO_4 type and is characterized by low mineralization (total dissolved solids <0.3 g L^{-1}), rather low pH (5.4), high oxidation-reduction potential (450–550 mV) and low content of total organic carbon (TOC < 1.5 mg L^{-1}).

2.2. Pilot test setup

The pilot test consisted of consecutive abiotic and biotic phases, where the application of nZVI was described in our previous work [13]. Briefly, the abiotic phase included the application of 120 kg (2 g L^{-1}) of nZVI (NANOFER 25, NANO IRON, Ltd., Czech Republic) in tap water. The nZVI suspension was applied to 3 different injection wells (Fig. 1) situated perpendicularly to the groundwater flow with a spacing of 2.8 m (an injected barrier configuration). The injection wells were encased with high-density polyethylene (HDPE) casing of 80 mm ID and were screened to the whole thickness of the aquifer (5–8.3 m below the ground surface). The amount of nZVI applied (2 kg nZVI ton^{-1} of soil) was previously assessed by laboratory tests of reduction of Cr(VI) by nZVI using the local soil and the groundwater. The biotic phase of the pilot test started approximately 9 months after the start of the first abiotic phase [13] in the same area. For even distribution of the substrate in the aquifer, a circulation system was installed comprising two injection wells (IN-1 and IN-2), two abstraction wells situated down-gradient (HV-218 and HV-219), a tank for the substrate and pipeline mains allowing dosing of the substrate into the groundwater via its pumping from the abstraction wells and recharging back to the aquifer through the injection wells (Fig. 2). The injection wells were installed as nested wells fitted with two HDPE casings of 63 mm in diameter. Each casing was immersed into different sections of the aquifer: 5–6.5 m and 7–8.5 m below ground level. The abstraction wells were encased with a 125 mm in diameter HDPE casing screened to a depth interval of 4–8 m below the ground surface.

Based on the results of laboratory batch tests, whey was selected as a substrate and was applied to the aquifer in amount of 5 m^3. The whey was continuously mixed with groundwater abstracted from the down-gradient wells in a volumetric ratio of 1:50 and injected back into the aquifer *via* the up-gradient injection wells (Fig. 2). The circulation of the groundwater treated with the substrate lasted 50 days. During this period injection/abstraction rates were periodically changed in order to achieve the most even distribution of the substrate within the circulation zone as schematically displayed in Fig. 2. When the circulation injection/abstraction of the groundwater was terminated, the natural groundwater flow was re-established and the groundwater monitoring continued for another 10 months. In total, the pilot test lasted ~21 months including both phases.

2.3. Monitoring

19 monitoring rounds were performed during the pilot test. During each the monitoring round, a series of groundwater samples was collected from seven different wells: three nZVI injection wells (PV-209, PV-213, PV-215) and three down-gradient monitoring wells (PV-214, PV-216, PV-217), where one up-gradient well served as a reference (PV-212). In addition, two other down-gradient wells (PV-201, PV-210) were sampled for only selected types of laboratory analyses (Fig. 1). The groundwater samples were collected after well purging using a submersible sampling pump Gigant (Ekotechnika, Czech Republic). Field parameters including the pH, oxidation-reduction potential, electrical