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Stability of biologically reduced chromium in soil

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ABSTRACT

A large number of previous studies demonstrate that bacteria are able to transform hexavalent chromium (Cr(VI)) to less toxic trivalent chromium that is stabilized within soil rather than dissolved in groundwater. However, concern persists about the long-term stability of the chromium in these insoluble forms. The goal of this study was to determine the stability of chromium within soil after biotreatment. Laboratory columns packed with highly contaminated soil from a chromium plating site were used to simulate in situ conditions. Molasses, nitrate, and/or sulfate were added to artificial groundwater (GW) in order to stimulate naturally occurring bacteria in the soil to transform Cr(VI). Carbon consumption, nitrate reduction, and hydraulic conductivity decreases provided evidence of bioactivity as the main cause of reduced effluent Cr(VI) compared to columns without carbon and/or nitrate addition. Subsequent flushing of the biostabilized soil for 12–15 days with unamended GW maintained effluent Cr(VI) below 100 μg/L compared to conditions without molasses addition where the effluent Cr(VI) concentrations always exceeded 655 μg/L. In batch tests after biotreatment, the soil was equilibrated with three different types of aqueous solutions in order to determine the stability of the chromium. Equilibrium aqueous chromium concentrations were the lowest from the soil that was removed from columns treated with carbon and nitrate addition. The results demonstrate that biological activity stimulated by carbon and nitrate addition resulted in significant chromium stabilization to forms that were not readily desorbed from the soil.

Introduction

Various industrial activities and waste disposal practices have resulted in the contamination of groundwater and soil with chromium [1]. In the environment, chromium is generally present in either the trivalent form, Cr(III), or hexavalent form, Cr(VI). Cr(VI) is the more toxic, soluble, and mobile of these species. The U.S. Environmental Protection Agency (EPA) has set a concentration limit for total chromium in drinking water at a maximum contaminant level (MCL) of 0.1 mg/L [2]. Some states and other countries have more stringent regulations on the allowable concentration levels of either total or hexavalent chromium, such as California [3] and World Health Organization [4] MCLs of 50 μg/L. California also has established a public health goal for Cr(VI) in drinking water of 0.02 μg/L [3].

Previous research has determined that various bacteria which are naturally present in soil and groundwater have the ability to transform Cr(VI) into Cr(III) [5–8]. Microbiological Cr(VI) reduction can occur due to its use as an electron acceptor [9,10], reduction via bacterial enzymes [11–13], or indirect reduction via by-products of bacterial activity such as hydrogen sulfide and Fe(II) [14,15]. This biotransformation results in a toxicity reduction. Due to the precipitation of various Cr(III) forms it can also cause stabilization that removes chromium from the groundwater. For example, Srivastava and Thakur [16] determined that a *Serratia* sp. transformed Cr(VI) into calcium chromium oxides, chromium fluoride phosphate and other organo-Cr(III) crystals. Column studies by Tokunaga et al. [17] where Cr(VI) reduction was effectively stimulated by carbon addition led them to propose biostimulation as an effective in situ remediation technique. Biobarriers have also been proposed for the containment of Cr(VI)-contaminated groundwater, on the basis of successful demonstration in laboratory-scale column experiments [18,19]. In situ bioremediation of chromium via injection of molasses, cheese whey, proprietary MRC® (Regenesis), and lactate has been reported in pilot studies and under full scale remediation, but the long-term stability of the chromium after active biostimulation ended was not reported [1,20–22].

It is important to determine the long-term stability of chromium in aquifer solids after biological treatment. Future dissolution or release of the chromium after biostimulation is

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completed must not exceed safe levels. Previous laboratory research determined that bioaugmentation with an iron-reducing microorganism that was added into soil that had been artificially spiked with chromium resulted in a 95–96% reduction in the amount of water soluble chromium that was measured by the EN12457-2 leaching test [23,24]. In another study that used unsaturated contaminated soil from a steel factory, indigenous bacteria that were biostimulated with tryptone and yeast extract reduced the water soluble Cr(VI) by 99.95% due to the conversion of Cr(VI) to carbonate-bonded Cr(III), iron and manganese oxide-bonded Cr(III), organic matter-bonded Cr(III), and other by-products [8]. However, it is unclear that the methods that were used to measure the water-soluble chromium in these studies provides a conservative estimate of chromium leachability out of the soil. These experiments mixed 1 part soil with 10 parts distilled water and mixed for only 24 h [24] or 1 h [8]. A different study provided strong evidence of the stability of bioreduced chromium due to the fact that heated acid digestion was able to recover only 40% of the original chromium from the soil after batch tests where sulfate and carbon amendment stimulated the anaerobic bio-transformation of Cr(VI) in contaminated site soil [25]. It is expected that different types of bioactivity (such as aerobic versus sulfate-reducing), soil type, and water chemistry will result in different chromium products and therefore differing long-term chromium stability.

The goal of this study was to determine what, if any, of four different biostimulation methods would achieve Cr(VI) biotransformation resulting in the long-term in situ stabilization of chromium. An experiment was designed to simulate in situ bioremediation conditions, and then two different methods were used to evaluate the stability of the chromium. First, whether aqueous chromium would remain below typical regulatory limits under "natural" conditions of groundwater flow as evaluated by passing unamended groundwater through the soil. Second, the amount of chromium that would be removed from the soil under batch equilibrium conditions with different "extraction" solutions was evaluated. The study results would reveal if any of the biostimulation conditions that were tested resulted in the production of stable forms of chromium in the biotreated soil.

Experimental

Soil

Chromium contaminated top soil (<15 cm deep) was collected from an active chrome plating facility located southeast of Denver, Colorado, and stored in clean plastic bags at 4 °C prior to use. The sandy soil averaged 44.6% gravel (2–5 mm), 23.2% coarse sand, 31.7% fine sand, and 0.5% silt plus clay by weight (per sieve analysis [26] and ASTM size classifications [27]). The specific gravity of solids was 2.5 g/cm^3 [28]. The soils had an average organic matter content (Method 1-4) of 4.6 ± 0.3% and pH of 8.04 (Method 12-2) [29]. The total chromium in the soil measured by acid digestion and permanganate oxidation (Standard Method 3030F and 3500D [30]) was 19,330 ± 4160 mg Cr/kg soil dry mass. X-ray powder diffraction and a Scintag PAD V was used to determine that the mineralogy of the soil was primarily quartz and feldspar. (The soil was turned into powder using a mortar and pestle and placed in a flat cuvette and placed into the PAD V. The counter was set to scan between 2 and 65 degrees of 2θ at a constant angular velocity of 2 deg/min. The Scintag software outputs mineral peaks and compares them to a database of known minerals.). The soil was also found to contain $3.0 \times 10^8 \pm 0.6 \times 10^8$ colony forming units (CFU) of aerobic bacteria per gram dry weight based on agar plating, described in the analytic methods below.

Biostabilization experiment

Laboratory columns were operated to simulate an in situ bioremediation approach. The columns were constructed as shown in Fig. 1 and operated as described previously in Bielefeldt et al. [31]. In brief, the chromium-contaminated site soil was packed into 15-cm long test columns and subjected to a continuous upflow of artificial ground water (GW) supplied by a peristaltic pump. The GW contained various carbon or nutrient amendments, as summarized in Table 1. The groundwater composition was based on Scholl et al. [32] and contained 1.5 mg/L KNO_3, 34.5 mg/L $MgSO_4{\cdot}7H_2O$, 12.0 mg/L $CaSO_4{\cdot}2H_2O$, 4.7 mg/L NaCl, and 1.2 mg/L $NaHCO_3$, at ionic strength 0.003 M (total 0.2 mg/L N and 20.5 mg/L SO_4^{-2}). This unamended GW was used in control columns 1 and 2. Supplemental nutrient addition in selected columns included 810 mg molasses/L (Brer Rabbit; measured total organic carbon, TOC, 194 mg/L; columns 4, 5, 6, 7, 8), 607 mg $NaNO_3$/L (100 mg N/L; columns 3, 5, 8), and/or 250 mg Na_2SO_4/L (169 mg/L as SO_4^{-2}; columns 3, 6, 7, 8). The pH was then adjusted to 6.8 and the water stored at room temperature (25 ± 2 °C) in a 4-L amber glass bottle. Effluent samples were collected from the outlet of the columns and analyzed for Cr(VI), nitrate-N, sulfate, and total Cr concentrations. Periodically, the pH, TOC, and heterotrophic bacteria in the effluent water were also measured.

Piezometers were attached to the sides of the columns to measure the head loss across the soil, from which the hydraulic conductivity was calculated. Decreases in the hydraulic conductivity were used as an indication of clogging of the soil with biomass and/or inorganic precipitates. The calculated average linear GW velocity in the columns was 0.8–1.8 m/d, resulting in a water residence time in the soil of 0.8–2.2 h.

After the effluent Cr(VI) concentrations from the biostimulated columns were stable at less than 0.1 mg/L (the US EPA MCL), the feed water was changed to unamended GW. The GW flushing was used to determine if the sorbed Cr within the columns was stable or if it would be flushed out once the biostimulation with carbon and nutrient addition was discontinued.

Chromium extraction tests

After the completion of the biostimulation experiments, the extractable chromium remaining in the soil was measured in batch tests. The columns were drained and the soil was sampled from various depths. Soil samples (~10 g dry weight) were placed in 40-

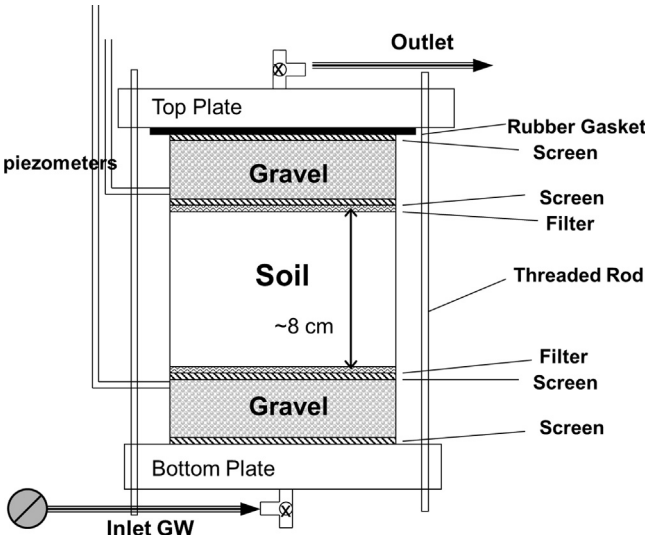

Fig. 1. Soil column test apparatus.