Journal of Hazardous Materials xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Using the natural biodegradation potential of shallow soils for in-situ remediation of deep vadose zone and groundwater

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HIGHLIGHTS

- Integrated in-situ remediation treatment for soil, vadose zone and groundwater.
- Turning the topsoil into an efficient bioreactor for perchlorate degradation.
- Treating perchlorate leachate from the deep vadose zone in the topsoil.
- Zero effluents discharge from the remediation process.

ARTICLE INFO

Article history:
Received 16 July 2016
Received in revised form 31 October 2016
Accepted 2 November 2016
Available online xxx

Keywords:
Soil flushing
In-situ remediation
Perchlorate
Vadose-zone monitoring

ABSTRACT

In this study, we examined the ability of top soil to degrade perchlorate from infiltrating polluted groundwater under unsaturated conditions. Column experiments designed to simulate typical remediation operation of daily wetting and draining cycles of contaminated water amended with an electron donor. Covering the infiltration area with bentonite ensured anaerobic conditions. The soil remained unsaturated, and redox potential dropped to less than −200 mV. Perchlorate was reduced continuously from ~1150 mg/L at the inlet to ~300 mg/L at the outlet in daily cycles. Removal efficiency was between 60 and 84%. No signs of bioclogging were observed during three operation months although occasional iron reduction observed due to excess electron donor. Changes in perchlorate reducing bacteria numbers were inferred from an increased in *pcrA* gene abundances from ~10^5 to 10^7 copied per gram at the end of the experiment indicating the growth of perchlorate-reducing bacteria. We proposed that the topsoil may serve as a bioreactor to treat high concentrations of perchlorate from the contaminated groundwater. The treated water that infiltrates from the topsoil through the vadose zone could be used to flush perchlorate from the deep vadose zone into the groundwater where it is retrieved again for treatment in the topsoil.

1. Introduction

Perchlorate is an environmental pollutant that is often attributed to ammonium perchlorate production in the explosives industry [1–3]. Its high solubility (220 g/l) and limited sorption to soil and sediments make it very mobile in the vadose zone and groundwater [4,5]. Perchlorate biodegradation in soils is possible under reducing conditions, in the presence of an electron donor and bacteria capable of perchlorate reduction [6–8]. The bacteria can use perchlorate as an alternative electron acceptor for metabolism in the absence of oxygen. Electron donor sources can be organic, such as acetate and ethanol, or inorganic, such as hydrogen gas [8,9]. The final byproducts of perchlorate reduction through the following general path—chloride and oxygen—are nontoxic: ClO_4^- (perchlorate) → ClO_3^- (chlorate) → ClO_2^- (chlorite) → Cl^- (chloride) + O_2 (oxygen) [9].

Although biodegradation of perchlorate in deep soils is feasible [6], from a technical standpoint, efficient performance in the natural deep unsaturated zone is a challenge. It requires: (a) maintaining reducing conditions and complete absence of oxygen, (b) a substantial supply of efficient electron donor to the deep part of the unsaturated zone, (c) maintaining sufficient moisture to sustain microbial community development, and (d) presence of indigenous perchlorate-degrading bacteria in the target horizons that are being subjected to the cleanup operation. Frankel and Owsianiak [10] succeeded to remediate a shallow vadose zone (3–13 m) contaminated with perchlorate at concentrations of 1–13 mg/kg using a high-pressure injection of corn syrup and ethanol. Evans

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http://dx.doi.org/10.1016/j.jhazmat.2016.11.003
0304-3894/

et al. [8] removed perchlorate at a concentration of ~75 mg/L from a contaminated vadose zone (3–12 m) using gaseous electron donor-injection technology. However, both cases demonstrated perchlorate-degradation capacity at relatively low perchlorate and salinity concentrations.

Leakage from waste water lagoons of an ammonium-perchlorate manufacturing plant by the area of Ramat Hasharon, Israel, has been resulted in heavy contamination of the vadose zone and groundwater [11,12]. In groundwater underlying the site the contaminated plum was found to spread over an area of several square kilometers with peak concentrations exceeding 1000 [mg/L]. The thick vadose zone underlying the former waste ponds (~40 m) was also found to contain extreme concentrations of perchlorate, exceeding 2200 mg/kg at depth of 20 m (equivalent to ~23,000 mg/L in the sediment pore-water) [1]. Attempts to enhance biodegradation of perchlorate in the vadose zone of that site included application of ethanol enriched water solution through a subsurface drip irrigation under a covered infiltration gallery [13]. A vadose zone-monitoring system (VMS) that was installed at the site enabled continuous monitoring of water infiltration, ethanol (electron donor) propagation, perchlorate degradation and solute transport across the entire vadose zone during the infiltration experiments (Supporting information Fig. S1 and S2) [14–16]. The results showed that while enhanced degradation of perchlorate was demonstrated at the upper soil layers, the efficiency of delivering high concentration of electron donor as ethanol, to deep sections of the vadose zone was limited, because it was consumed rapidly in the top soil. In addition, temporal variation of perchlorate concentrations across the vadose zone indicated significant displacement of perchlorate from the vadose zone toward the groundwater with the percolating water [13]. Later investigation of the microbial potential for perchlorate degradation in sediments from the vadose zone of the site suggested high reduction activity in the shallow soils and only limited and bio reduction potential at the deep highly contaminated layers (Supporting information Fig. S3, [12]).

A possibility to overcome the above limitations on in-situ bio degradation of perchlorate in deep vadose zone is through hydraulic flushing and leaching [17]. Nevertheless, this method requires recovery of the contaminated extraction fluids from the underlying aquifer for treatment and recycle, when possible. The recovered solution is usually treated above ground in engineered industrial facilities and then discarded into the local sewer system. For example, a pilot soil flushing from perchlorate was proposed for unsaturated soil at Tronox's Henderson facility, located in Southern Nevada [18,19].

Here we propose an alternative approach for remediation of the deep vadose zone and decontaminate polluted groundwater using the bio reactive part of the soil. In this approach contaminated groundwater is pumped through a series of shallow wells tapping the upper groundwater (Fig. 1). The contaminated groundwater is than enriched with electron donor and reintroduced top soil for treatment. The treated water percolated gravitationally through the vadose zone and leach pollutants to the groundwater where it is retrieved back for treatment in the top soil through a cyclic process. The main advantages this remediation approach are: (a) it exploits the high degradation potential and accessibility of the top soils and saves substantially on expensive engineered infrastructure, (b) it treats large volumes of ambient contaminated groundwater without introducing additional chemicals which may affect the aquifer's hydraulic properties [20,21], (c) it does not require large capital investment for the construction and operation of external treatment facilities, making this remediation process cost-efficient, and (d) it does not involve further contamination with polluted effluents. Upon combination of the remediation approach with application of vadose zone monitoring technologies the method may be optimized by a real-time indication of the actual transport and degradation activity of the unsaturated zone microbial communities.

While the leaching and pumping phases of the proposed treatment approach are well established in the literature [17], including results from previous stages for our study site [13], in the current study we focus on the first phase of the suggested remediation treatment: degradation of perchlorate in the upper unsaturated soil layers of the contaminated site. Degradation capacity was investigated through long-term column experiments, where synthetic contaminated groundwater was applied continuously to unsaturated columns of local soil for bio treatment.

2. Materials and methods

The potential capacity of shallow soils to serve as a bio reactor for continuous treatment of perchlorate was tested through long-term column-infiltration experiments. Two main practical aspects guided the design of the column experiment: (a) maintaining unsaturated flow conditions in the entire soil column, as expected in the unsaturated zone [22,23], and (b) continuous treatment of percolating water that imitates the local groundwater, heavily contaminated with perchlorate, with the addition of excess electron donor.

2.1. Column design and treatment application

We believe that the most suitable way to apply the suggested treatment in the field is by subsurface drip irrigation. Such irrigation systems allow accurate control of the water-application cycles as well as the chemical composition of the implemented water. Accordingly, the columns were designed to represent the coverage area of a typical commercial dripper with a discharge rate of 2.5 L/h. The dripper was placed in the center of the column with radius of influence of 21 cm to represent a typical dripper's distribution of 30 × 30 cm in the field. The use of subsurface irrigation under impervious cover was expected to encourage the generation of reducing conditions, which are an essential prerequisite for successful biodegradation of perchlorate.

Three large polyethylene columns (42 cm diameter, 55 cm height) were packed with soil from an area that was used in the past as a waste pond [6,12] (Fig. 2). The soil was collected from the upper 50 cm of the profile at three different locations, to reflect the local heterogeneity. Prior to packing, the soil was mixed and sieved with a coarse mesh (1 mm) to eliminate roots and stones. The soil texture (95% sand, 2.5% silt and 2.5% clay) was determined by hydrometer method [24]. During packing, the soil was physically compacted to prevent the formation of large unnatural voids. An infiltration gallery was constructed at the top of the column with a 2-cm layer of coarse tuff (1–10 mm). Initially the infiltration gallery was covered with a polyethylene sheet which was found inefficient at creating reducing conditions. As a result, later in the experiment, the cover was replaced with 2-cm thick layer of bentonite, which was found suitable for isolating the column from atmospheric oxygen (Supporting information Fig. S4).

To maintain the unsaturated conditions that prevail in natural unsaturated zone, the drainage system was designed to create low tension at the outlet of the column; a 2-cm thick rockwool layer was placed at the bottom of each column [25]. The outlet was extended with a 60-cm long pipe filled with compressed rockwool, which created hydraulic continuity and resulted in light tension that resembled the conditions in an unsaturated profile [25]. The bottom of the drainage extension was connected to a syphon made of a 6-mm diameter tube to prevent air penetration into the column.