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Effect of soil composition on electrokinetically enhanced persulfate oxidation of polychlorobiphenyls

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ABSTRACT

In situ oxidation processes for the remediation of organic contaminants in soils have gained much interest in last decade. They are rapid, aggressive and easy to apply, but their application in low permeability soils is limited due to the ineffective delivery of oxidants in such soils. In this study, electrokinetically enhanced persulfate delivery and oxidation is investigated in two diverse low permeability soils: artificially contaminated kaolin and glacial till soil. These two soils were used to investigate the effects of soil type on persulfate oxidation of tetrachlorobiphenyl (PCB 44), a representative polychlorobiphenyl (PCB). Laboratory batch tests were conducted using the soils spiked with PCB 44 at an initial concentration of 50 mg/kg to determine the optimal conditions for effective oxidation. This study also investigated the activation of persulfate by elevated temperature (45 °C) and high pH (at anode) as a means to maximize PCB degradation. The activation of persulfate improved the oxidation of PCB in kaolin, but the effect in the glacial till was insignificant. The final pH values of the kaolin were around 1, while they were around 7 for glacial till because of the high buffering capacity of glacial till. Low pH conditions are also shown to activate persulfate, leading to higher PCB oxidation. The degradation of PCB 44 was significantly higher for the kaolin than the glacial till. In kaolin, the highest level of PCB oxidation, 77.9%, was achieved with temperature activated persulfate in 7 days. However, in the glacial till the highest PCB oxidation was 14.4% with 30% Na-persulfate concentration without any activation. The high buffering capacity, non-homogeneous mineral content and high organic content of glacial till may have contributed to the low persulfate oxidation of PCB.

1. Introduction

The destruction of organic contaminants, particularly recalcitrant polychlorobiphenyls (PCBs), in soils has been one of the environmental challenges during the last decade. PCBs are a group of chlorinated compounds which may cause adverse reproductive effects, developmental toxicity, and cancer, and, thus, are dangerous to human health and wildlife [1]. PCBs are non-polar compounds that are only slightly soluble in water (highly lipophilicity) and strongly adsorb to soils, which makes them persist in the soils [2,3].

There are several methods for remediation of PCB-contaminated soils, such as incineration, thermal desorption, chemical dehalogenation, solvent extraction, soil washing, solidification/stabilization, and vitrification [4]. However, each of them has some disadvantages when used for remediating PCBs. For example, while incineration at high temperature is a widely used technology for treating soils and sediments contaminated with PCBs, there is a potential danger for the release of dioxins via the flue gas stream [4]. Some of the remediation methods are also sensitive to soil grain-size, clay content, and soil pH, and are ineffective for the complete remediation of heavily contaminated soils [5]. For soil washing and incineration methods, soil grain size and moisture content are important parameters for implementing of these methods [4].

In situ chemical oxidation has gained much interest during the last decade; it consists of the injection of chemical oxidants into contaminated soils and groundwater to oxidize the contaminants [5,6]. Chemical oxidation is a rapid, aggressive process, simple to use and can be applied in situ avoiding the need to disturb the ground structures or undertake expensive excavation procedures. Hydrogen peroxide, Fenton's reagent, permanganate, and ozone are widely used oxidants, but their chemical stability and fast reaction are a hindrance to practical applications [7]. Persulfate is a strong

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Table 1
Properties of kaolin and glacial till soils used in this study.

Property	Kaolin	Glacial till
Mineralogy	Kaolinite: 100%	Quartz: 31% Feldspar: 13% Carbonate: 35% Illite: 15% Chlorite: 4–6%
Particle size distribution (ASTM D422)		
Sand (4.75–0.075 mm)	4%	20%
Silt (0.075–0.002 mm)	18%	44%
Clay (<0.002 mm)	78%	36%
Liquid limit (ASTM D2487)	50%	21.7%
Plasticity index	22.6%	10.0%
Specific gravity (ASTM D854)	2.6	2.71
pH (ASTM D4972)	4.9	8.2
Cation exchange capacity (meq/100 g) (ASTM D9081)	1–1.6	13–18
Organic content (ASTM D2974)	~0	2.8%

oxidant (oxidation potential about 2.0 V) and kinetically slow in destroying many types of organic contaminants [5]. Also, persulfate has longer life in the subsurface as compared to hydrogen peroxide and ozone [7]. Moreover, if activated, persulfate can be decomposed into sulfate radicals ($SO_4^{\bullet}$), which are very powerful and kinetically fast oxidants [5,8]. The sulfate radicals have a standard redox potential of 2.6 V and may able to oxidize many types of organic contaminants [9]. There are four primary methods for activation of persulfate: heat, metal chelates, hydrogen peroxide, and high pH [7,8,10]. Selecting the suitable activator depends on the site conditions such as lithology (clay, sand, etc.), hydrogeology, and the application method [4,8].

The reactions of persulfate ions with various organic and inorganic compounds have been studied by several researchers [5,7,9]. In one study where heat assisted persulfate oxidation was used for the remediation of methyl tert-butyl ether (MTBE) in contaminated groundwater, it was found that use of persulfate instead of Fenton's chemistry and ozonation is advantageous because of persulfate's higher stability in the subsurface [7]. Persulfate may be oxidized using different approaches, including iron, elevated temperature and/or very low or high pH conditions, for enhanced oxidation efficiency. For example, when activated sodium persulfate was used to degrade poly-aromatic hydrocarbons (PAHs) in sediment, the remedial efficiency improved to 90%; however, when activated persulfate and hydrogen peroxide were combined, the removal of total PAHs only increased to 92% [5]. In a different study [2], Fe(II) mediated activation of persulfate was used for the remediation of PCBs in aqueous and sediment systems with a 54% removal for 2-chlorobiphenyl.

Due to its relatively high stability under normal subsurface conditions, non-activated or activated persulfate can effectively travel through the subsurface into the contaminated zone during in situ remediation applications. Major advantages of persulfate when compared to other oxidant systems are high chemical stability, low affinity for natural soil organics (less than permanganate ion), increased transport distances in subsurface and fast reaction when activated. In addition to these advantages, persulfate possesses high aqueous solubility, has relatively low cost and results in benign end products (sodium and sulfate) [7]. As a strong oxidant, it will break-up the organic contaminants, including biphenyl ring, and cleave the aromatic ring, resulting in smaller and non-toxic organic fragments after oxidation [7]. Complete oxidation will result in the formation of CO_2, H_2O and Cl^-. Partial oxidation of PCBs is shown to result intermediate products such as lower chlorinated PCB congeners (3,3′,4- and 3,4,4′-TriCB; 3,3′-, 3,4-, 3,4′-, and 4,4′-DiCB; and 3- and 4-CB), biphenyl, CO, and CO_2 [11].

The integration of chemical oxidation with electrokinetic remediation has the potential to increase delivery and improve the remedial efficiency of soils contaminated with organic contaminants in low permeability clayey soils [12]. However, the delivery and extent of oxidation may depend on the composition of clayey soils, which has not been investigated to date. In particular, the effects of organic matter content and mineralogy of the clayey soils on persulfate oxidation efficiency has not been investigated. It was reported that electrokinetically enhanced oxidation with sodium persulfate resulted in better PAH removal (35%) than either electrokinetics (24%) or persulfate oxidation (12%) alone [9]. The aim of this study was to evaluate the effect of soil composition, particularly low permeability soils, on electrokinetically enhanced persulfate oxidation without and with heat and high pH activation for remediation of PCBs.

2. Experimental

2.1. Materials

Kaolin and glacial till were used to represent two low permeability soils with different mineralogy characteristics. Kaolin has a low organic content, consistent and uniform mineralogy, is fairly nonreactive, and has a low cation exchange capacity (Table 1). Hence, kaolin is a good control soil for laboratory electrokinetic testing because the amount of experimental variation as a result of soil heterogeneity is minimized and the influence of variables such as oxidant dosage during the electrokinetic treatment can be drawn easily. Glacial till, on the other hand, is a highly variable soil with a relatively high organic content, complex mineralogy, and particle size distribution. The glacial till is more representative of the field soils encountered in the Midwestern United States. The properties of the kaolin and glacial till used in this study are shown in Table 1.

PCB 44 (2,2′,3,5′ tetrachlorobiphenyl) was used as a representative PCB ($C1_2H_6C_{14}$) and was obtained from Ultra Scientific (North Kingston, RI). Its purity is higher than 97%. Sodium persulfate ($Na_2S_2O_8$ >99%) was obtained from FMC (Philadelphia, PA). Reagent grade acetone was obtained from Fisher Scientific (Fair Lawn, NJ).

2.2. Batch oxidation tests

Several series of batch oxidation tests were conducted to determine the most effective parameters on the PCB degradation. The effects of activators (temperature, pH), reaction time and persulfate dosage on oxidation of PCB were investigated. The kaolin and glacial till samples were spiked each with PCB at an initial target concentration of 50 mg/kg. Prior to spiking, the required mass of PCB was completely dissolved in hexane and then mixed with the soil with additional hexane in such manner that the soil–PCB–hexane mixture could easily be blended homogenously. The mixture was stirred for 20 min using stainless steel spoons in glass beakers. The soil–PCB–hexane mixture was then placed in a ventilation hood for nearly 10 days until the hexane evaporated completely. The spiked soil was analyzed to determine the exact initial PCB contaminant concentrations.

For each batch oxidation test, 1 g of dry contaminated soil was placed in a 50 mL centrifuge tube. About 10 mL of Na-persulfate solution was added to the tube to produce a soil–liquid mixing ratio (S/L) of 1:10. Sulfuric acid was used to adjust the pH to a predetermined value of 2 and 4. The soil and persulfate solution were mixed in a mechanical shaker for predetermined reaction time (1–7 days). At the end of the reaction time, the soil and supernatant solution were separated by centrifugation at 6400 rpm for about 10 min. The soil was then solvent extracted with acetone for 24 h to determine the residual PCB concentration. Several series of batch experiments