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Remediation HCHs POPs-contaminated soil by activated persulfate technologies: Feasibility, impact of activation methods and mechanistic implications

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ABSTRACT

Hexachlorocyclohexanes (HCHs) waste stockpiles are the single largest source of POPs. Sites contaminated with high levels of HCHs pose serious threats to public health and environmental safety, but there remains a lack of proper environmentally sound solution. To provide guidance on this issue, the remediation of contaminated soil with high levels of γ-HCH (~800 mg/kg) by persulfate with three commonly applied field activation methods, namely heat activation at 40 °C, high pH and Fe(III)-EDTA activation, was investigated. The effects of activation method and persulfate dosage on the degradation and dechlorination of γ-HCH were studied, and degradation pathways were proposed. The results show that heat-activated persulfate is highly effective for the remediation of γ-HCH, achieving complete degradation and dechlorination of γ-HCH in 14 days. Under high pH conditions, γ-HCH rapidly dehydrochlorizes into trichlorobenzenes, which are further degraded by persulfate. On the other hand, persulfate alone at 20 °C and Fe(III)-EDTA activated persulfate are not effective for the degradation of γ-HCH, due to limited generation of reactive radical species resulting from the inefficient activation of persulfate, and the competition of soil organic materials and Fe(III)-EDTA with γ-HCH for reactive radicals.

1. Introduction

Technical hexachlorocyclohexanes (HCHs) and the purified gamma isomer of HCHs (γ-HCH, Lindane) are among the most widely produced and used pesticides, with an estimated total global production of over 10 million tons [1]. The production of HCHs, dumping of HCHs isomer waste and storage of unused stockpiles have resulted in numerous seriously contaminated sites all over the world [2–5]. These sites normally have shockingly high levels of HCHs contamination and remain continuous point sources of HCHs, contaminating the groundwater, volatizing into the air, transferring to the food chain and posing serious threats to the public health and environmental safety [4]. For example, the surface soil of a production site in Spain has total HCHs with a mean level of over 1000 mg/kg and a maximum concentration around 20,000 mg/kg [6]. As HCHs have neurological, renal, hepatic, immunological, and reproductive toxicities, and are carcinogenic [4,5], their existence in the environment has raised global concerns, resulting in α-HCH, β-HCH and γ-HCH being listed as POPs in the Stockholm Convention in 2009 [7]. It is estimated that 4.8–7.2 million tons of HCHs waste exist worldwide [7], making HCHs the largest single POPs stockpile with the overall quantity exceeding all other POPs wastes combined, and posing great challenges for environmentally sound management of the POPs waste.

The Stockholm Convention mandates an irreversible destruction or transformation of POPs into non-POPs compounds. Traditionally, concentrated POPs have been mainly treated by incineration at high temperature. But concerns over the potential production of secondary contaminants, especially dioxins and furans, have resulted in strong public opposition to the application of combustion technologies. In addition, the strict requirements for equipments and procedures for the safe disposition of POPs by incineration at high temperature also create enormous burdens and challenges for developing countries, both economically and technologically, where most HCHs wastes are located [8]. Therefore, development of cost-effective, safe and environmentally sound non-combustion technologies for the destruction of POPs is crucial for the management of POPs contaminated sites.

In Situ Chemical Oxidation (ISCO) is an emerging technology [9] that offers a promising solution for the safe remediation of sites/soil contaminated with high levels of POPs, including HCHs. In ISCO, environmental friendly oxidants are applied to the subsurface to oxidize the contaminants of concern into carbon dioxide

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or other less toxic products [9]. Permanganate, Fenton's reagent, and persulfate have been generally applied in ISCO [10]. Permanganate is a relatively weak oxidant normally applied for the oxidation of chlorinated ethylenes, but it generally has limited effectiveness for other recalcitrant organic contaminants. Fenton's reagent is highly reactive toward most recalcitrant organic contaminants, but its instability in the subsurface raises great concerns over safety issues and the potential escape of HCHs through volatilization, etc., as rapid decomposition of hydrogen peroxide may generate large amounts of heat and gas in the subsurface [11]. Sodium persulfate is a newer but increasingly used oxidant for ISCO [12] in the last decade, favored by its stability, convenience of application by injecting a high concentration solution to the subsurface, larger radius of impact and a much longer lifetime in the subsurface than hydrogen peroxide, etc. [12,13].

Sodium persulfate normally needs to be activated in the subsurface to generate reactive radical species, mainly sulfate radical ($E^0 = 2.6$ V) and hydroxyl radical ($E^0 = 2.7$ V), which can oxidize most recalcitrant organic contaminants [12]. But superoxide anion radicals can also be generated and play a crucial role in the destruction of chlorinated alkanes [14–16]. Of the numerous activation methods, heat-activation, Fe(III)-EDTA activation and high pH activation are most frequently applied in field remediation projects, due to their applicability to the subsurface and extensive engineering experiences [12].

To the best of our knowledge, the interaction between persulfate and HCHs, especially concentrated HCHs in soil, has rarely been studied. Previously, Zhang and co-workers [17] studied the oxidation of γ-HCH (5 mg/L) in deionized water by ferrous ion catalyzed persulfate, and Crimi [18] reported the persulfate oxidation of HCHs in two groundwater samples (7 and 630 μg/L, respectively) by heat activation, hydrogen peroxide activation, ferrous sulfate/EDTA activation and high pH activation. Both aqueous studies indicate that activated persulfate is effective for the mineralization of dissolved HCHs in low concentrations. Recently, Usman and co-workers [19] studied the treatment of HCHs contaminated soils with Fenton's reagent, permanganate oxidation, persulfate alone and Fe(II)-EDTA activated persulfate, showing limited effectiveness by persulfate processes. These studies demonstrate that the mineralization of high levels of HCHs in soil by activated persulfate is much more complicated than that of low levels of HCHs in homogenous aqueous solutions, potentially due to the adsorption of hydrophobic organic contaminants by soil [20], consumption of oxidants by natural organic matter and other reducible species, limited mass transfer in the heterogeneous system, etc. [9]. Considering that the remediation of HCHs contaminated soil with persulfate activated by the three commonly applied field processes, namely heat activation, Fe(III)-EDTA activation and high pH activation, has not been investigated before, this study thoroughly studied the persulfate oxidation of high levels of γ-HCH in spiked soil samples (~800 mg/kg), to mimic soils from highly contaminated sites, with these three activating conditions in order to provides fundamental and practical knowledge for the remediation of HCHs contaminated sites with activated persulfate.

The main objectives of the current study are to (1) establish the feasibility of using activated persulfate for the remediation of contaminated sites with high levels of HCHs; (2) evaluate the impact of activation methods on the destruction of HCHs and elucidate the potential underlying mechanisms by examining the interaction between HCHs and the reactive species generated under each condition, potential influence of soil matrix, etc.; (3) determine potential degradation pathways of HCHs with special focus on the impact of activation methods on the degradation pathways; and (4) identify proper conditions to achieve effective remediation of HCHs contaminated soil. Overall, the study provides valuable guidance for the management of not only HCHs, but also another class of emerging POPs, short-chain chlorinated paraffins [21], which are also highly chlorinated alkanes and whose management information is currently lacking.

2. Materials and methods

2.1. Materials

γ-HCH analytical standard (98.5%) was from Dr. Ehrenstorfer GmbH, Germany. Sodium persulfate (98%), ceric sulfate (99.9%), ammonium iron sulfate hexahydrate (99%), anhydrous sodium sulfate (99%), anhydrous sodium hydrogen sulfite (99%), sulfuric acid (98%) and sodium hydroxide (98%) were all analytical grade and used as received. Acetone, hexane and methyl *t*-butyl ether (MTBE) were HPLC grade. N,O-bis(trimethylsilyl)trifluoroacetamide/trimethylchlorosilane (BSTFA-TMCS; v/v, 99/1) was employed to derivatize potential γ-HCH degradation intermediates for GC–MS analysis. Milli-Q ultra pure water was used to prepare all aqueous solutions.

2.2. Persulfate oxidation of γ-HCH in spiked soils

The soil samples used were typical lateritic red soils obtained from Guangzhou, China at a depth of 20–40 cm. The soil was dried in the lab and then grinded to pass a 35-mesh sieve. The properties of the soil were previously determined and reported [22] as containing approximately 66% well graded sand (<2 mm), 14% silt and 20% clay, with a pH of ~5.45, an organic content of ~0.25 wt% and an iron content of ~3.3 wt%.

γ-HCH spiked soil samples were prepared as follows: 1200 g soil was placed in a 1000-mL flask and spiked with ~1000 mg γ-HCH dissolved in ~100 mL of acetone, followed by the addition of more acetone to thoroughly submerge the soil. The soil was then stirred mechanically vigorously for 30 min to promote homogeneous distribution of γ-HCH. Acetone was then evaporated by allowing the sample to rest for 3 days under a fume hood, with frequent mechanical stirring to promote homogenous distribution of γ-HCH. Thereafter, the soil was thoroughly mixed and aged for one month in the fume hood till use. The initial γ-HCH concentration in the soil was determined to be ~800 mg/kg as follows: 1.0 g spiked soil in 40-mL EPA VOA vials was sonicated for 30 min with 10 mL acetone/hexane (1:1, V/V) in an ultrasonic bath (40 kHz/600w), followed by GC/FID analysis of the upper organic layer.

The degradation experiments were conducted in 40-mL EPA VOA vials, sealed with open-top caps with Teflon-lined septa. Prior to each experiment, 5.0 g spiked soil was added to the vials, followed by the addition of 20 mL solution with sodium persulfate and designated activators at desired concentrations as specified in Section 3. The vials were then kept in incubators maintained at 20 °C or 40 °C, respectively, in the dark, and shaken at ~200 rpm. Blank control without oxidants or activators was also run at 20 °C and 40 °C, whereas additional control with only NaOH was run for high pH activation. All experiments were conducted in duplicates.

2.3. Sample workup procedures

At pre-specified time intervals, the sample vials were immediately put into an ice-water bath to quench the reaction for ~10 min. Thereafter, the samples were centrifuged to separate the aqueous phase from the soil phase. The upper aqueous phase was transferred to a clean 40-mL vial, and pH was recorded. 10 mL ultra pure water at ambient temperature (~20 °C) was then added into to the original reaction vial and the soil particles were thoroughly redispersed with the assistance of a hand-held high