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Efficient chemical oxidation of high levels of soil-sorbed phenanthrene by ultrasound induced, thermally activated persulfate

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HIGHLIGHTS

- Ultrasound induces thermal activation of persulfate.
- Persulfate oxidation is mainly responsible for the destruction of organic contaminants.
- Ultrasound facilitates desorption of HOCs and mass transfer of oxidants in heterogeneous environment.
- Ultrasound promotes highly efficient oxidation of soil-sorbed phenanthrene.
- Coupling downhole ultrasound technology with persulfate process was proposed for in situ remediation.

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ABSTRACT

The sorption of hydrophobic organic contaminants (HOCs) and limited mass transfer in heterogeneous subsurface environment are major hurdles to efficient remediation of highly contaminated sites by traditional activated persulfate. In this work, ultrasound was coupled to persulfate oxidation to enhance the remediation. The mechanisms of the coupling process were investigated, using soil spiked with high levels of phenanthrene as a model compound for PAHs and other HOCs. The results indicate that, when ultrasound is applied to the soil slurry, the resultant heat, due to the ultrasonic energy absorbed by the soil particles, activates persulfate to generate sulfate radicals to oxidize the dissolved phenanthrene, and the dissolution and desorption of the phenanthrene are also enhanced by elevated temperature, ultrasound itself and the oxidation by persulfate, thereby creating a positive-feedback loop that induces rapid and highly efficient oxidation of the contaminants. Furthermore, the effects of ultrasound intensity, contaminant concentration, oxidant dosage, soil to water ratio, and addition of external activators on the oxidation of phenanthrene were also studied. For potential field applications, coupling downhole ultrasound technologies with traditional persulfate process was proposed to facilitate the remediation of HOCs contaminated sites.

1. Introduction

In situ chemical oxidation (ISCO) is increasingly used for the remediation of soil and groundwater containing organic contaminants. ISCO normally utilizes environmentally friendly oxidants, such as permanganate, hydrogen peroxide and persulfate [1,2]. Permanganate is mainly used for the oxidation of chlorinated ethenes, while catalyzed hydrogen peroxide and activated persulfate can oxidize most recalcitrant organic contaminants through the generation of highly reactive radical species, including hydroxyl radicals and sulfate radicals that are highly oxidative and reactive toward most organic contaminants. Superoxide anion radical species can also be generated in the latter two oxidation systems, and it is a weak oxidant, but effective reductant toward chloroalkanes, such as carbon tetrachloride and hexachloroethane that are recalcitrant toward oxidation [1–3]. Of these two general oxidants, persulfate is increasingly used in field projects in the last decade because of its higher stability in subsurface, longer lifetime and larger radius of influence, etc., compared to hydrogen peroxide [1–3].

Activated persulfate is normally applied for the treatment of source zones (hot spots with high levels of contamination) [1–3], but its field applications have encountered serious challenges, especially for the treatment of hydrophobic organic contaminants (HOCs) [4], due to the their generally low aqueous solubility and the sequestration of HOCs by soil aggregates (Scheme 1). Adsorption of HOCs to mineral surfaces, absorption onto flexible/soft natural organic matter, adsorption on hard/condensed natural organic

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matter, diffusion in micro-porous media, and encapsulation by mineral coating are the main mechanisms accounted for the sequestration of HOCs, with the first two mechanisms being usually fast and reversible, whereas the latter three exhibiting slow desorption and irreversible sequestration of HOCs [5], which can seriously hinder the oxidation of HOCs, assumed to occur in the aqueous phase. Furthermore, in a heterogeneous subsurface environment, the preferential delivery of reagent solution to relatively more permeable zones may result in oxidant bypassing contaminants located in less permeable zones [6], while limited intra-aggregate mass transfer further hurdles the diffusion of oxidant solutions to target contaminants sorbed inside mesopores or micropores of the soil aggregates [7]. Due to the above mentioned factors as well as the self-decomposition of persulfate, consumption of oxidants by other readily oxidizable soil materials, etc. [1–3], unsuccessful or incomplete destruction of HOCs in field projects employing activated persulfate has been frequently documented [8], even though bench top studies in aqueous solutions and slurry systems under intense mixing or shaking have demonstrated the potential of activated persulfate for the remediation of HOCs-contaminated sites [9].

To enhance the desorption rate of HOCs and the mass transfer in heterogeneous subsurface, this study coupled ultrasound with persulfate for the oxidation of high-level soil-sorbed HOCs. When ultrasound is introduced into the subsurface environment, the induced physical effects, including microstreaming, microstreamers, microjects, shockwaves, etc. [10,11], can facilitate intensive mixing, breaking of soil aggregates, the desorption and diffusion of HOCs from the soil aggregates to the bulk, transfer of oxidant from the bulk into soil aggregates, the delivery of oxidant to less permeable areas, etc. As a result, the contact between the oxidant and the contaminants is expected to be substantially enhanced, resulting in more efficient and complete destruction of organic contaminants in complex heterogeneous subsurface environments.

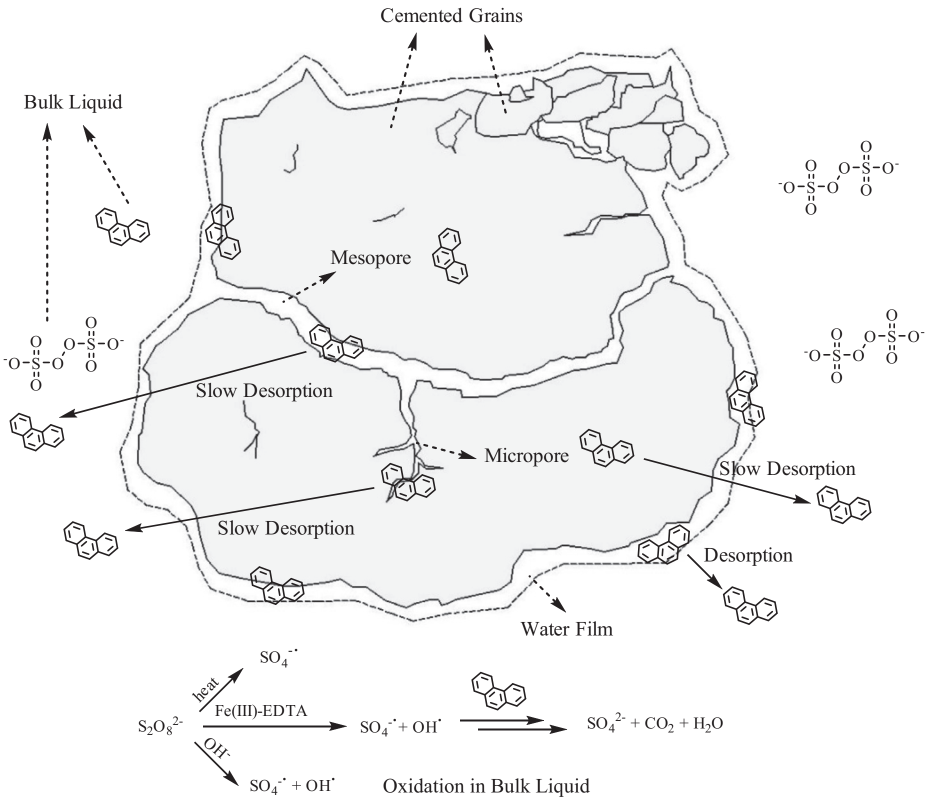
In addition, previous studies indicate that ultrasound can effectively activate persulfate [12], thereby offering an alternative persulfate activation route which may avoid the addition of external activators/activations, such as heat-activation at ~40 °C, Fe(III)–EDTA activation and high pH activation (e.g. addition of NaOH) that are most frequently applied in field projects [3]. Consequently, this may lead to the reduction of chemical and engineering costs. Theoretically, ultrasound can also oxidize organic contaminants through the generation of highly reactive radicals or pyrolysis, but the effect is expected to be seriously impaired by the subsurface matrix [13–15], reconfirmed by results from this study.

The current study investigated the fundamental mechanism of the coupling process using soil spiked with high levels of phenanthrene as a model HOCs compound. The results show that the coupling process can result in highly efficient oxidation of soil-sorbed phenanthrene, with ultrasound inducing thermal activation of persulfate and enhancing the desorption of phenanthrene. The influence of operating parameters, including ultrasonic power intensity, persulfate concentration, contamination level, soil to water ratio and addition of external activators, on the oxidation of phenanthrene was studied. In addition, the downhole ultrasound technology, which has been extensively investigated to enhance oil well production but rarely explored for soil remediation, was proposed to couple with traditional persulfate oxidation to facilitate site remediation.

2. Experimental

2.1. Materials

Phenanthrene (99.5%) and naphthalene (99.7%) analytical standards were from Sigma–Aldrich, USA. Sodium persulfate (98%),



Scheme 1. Schematic of activated persulfate oxidation of soil sorbed-HOCs. The oxidation of HOCs is usually limited by their availability in the bulk liquid phase, due to their low aqueous solubility, slow desorption to the bulk liquid, encapsulation by inorganic minerals, etc.