

DEPTH OF FENTON-LIKE OXIDATION IN REMEDIATION OF SURFACE SOIL

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ABSTRACT: A series of soil columns was used to investigate the depth of Fenton-like reactions provided by the surface application of catalyzed hydrogen peroxide. Initial experiments examined the effect of four stabilizers (monobasic potassium phosphate, dibasic potassium phosphates, sodium tripolyphosphates, and silicic acid) on H₂O₂ decomposition and the depth to which H₂O₂ could be detected. The H₂O₂ dynamics along the depth of the column showed that the addition of the most effective stabilizer, monobasic potassium phosphates, increased the depth of the detectable H₂O₂ in the soil by three times the depth in soil columns without stabilization. The oxidation of sorbed hexadecane, a highly hydrophobic compound (log K_{OW} = 9.07), by Fenton-like reactions focused on the process variables of H₂O₂ concentration, number of H₂O₂ applications, and pH. A single application of 15 M H₂O₂ with pH governed by the buffering of KH₂PO₄ provided maximum hexadecane oxidation. Minimal desorption (<10%) in the soil columns was found in control experiments using deionized water in place of H₂O₂ suggesting that hexadecane oxidation occurred in the sorbed phase. More detailed investigation of the process variables was conducted using central composite rotatable designs. The results showed that a KH₂PO₄ concentration greater than 30 mM provided increased hexadecane oxidation while maintaining minimal H₂O₂ decomposition relative to unstabilized H₂O₂. For higher KH₂PO₄ concentrations (60-75 mM), the central composite results documented greater than 90% hexadecane oxidation in the top 2 cm of the soil column and 20-40% oxidation in the 10-15 cm depths.

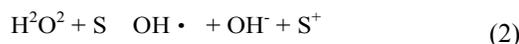
INTRODUCTION

The remediation of contaminated soils is a significant problem because they are a complex media and many contaminants are sorbed, resulting in decreased availability to biochemical or physiochemical transformations. The use of Fenton's reagent to remediate contaminated soils has recently received increased attention because of its ability to oxidize a wide range of contaminants. The process is well documented (Walling 1975) and involves the decomposition of H₂O₂ catalyzed by iron (II) or other transition elements leading to hydroxyl radical production.



Hydroxyl radicals are nonspecific oxidants that react with most organic contaminants at rates close to their theoretical limit which is controlled by the rate of diffusion in water [$\sim 10^{10}$ l/(M.s)].

Early work on the use of Fenton-like processes for the remediation of contaminated soils focused on the addition of excess reagents iron (II) and H₂O₂. Watts et al. (1990) documented the mineralization of high concentrations of pentachlorophenol (PCP) using 7% H₂O₂ and 8 mM iron (II) at pH 3. Perchloroethylene (PCE) and octachlorodibenzo-*p*-dioxin (OCDD) were also oxidized using similar process conditions (Watts et al. 1991; Leung et al. 1992). Tyre et al. (1991) investigated the Fenton-like oxidation of four contaminants in soils and found that the more hydrophobic compounds were oxidized slowly with higher stoichiometric H₂O₂ requirements. Tyre et al. (1991) also hypothesized that the natural iron oxyhydroxides present in the soil may be capable of catalyzing the Fenton-like reactions:



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where S = surface of the iron mineral. Watts et al. (1993) compared the catalysis of H₂O₂ by iron oxyhydroxides to the standard Fenton's technique and the addition of excess reagents, and found that the iron oxyhydroxides provided the most efficient stoichiometry (i.e. moles contaminant degraded/mole H₂O₂ consumed).

The application of catalyzed H₂O₂ under in situ-conditions for oxidizing sorbed contaminants may be limited by the instability of the H₂O₂ in the system and sorption of the contaminants. When added to soil, H₂O₂ is unstable due to the presence of inorganic and organic reactants (Britton 1985). Inorganic reactants include catalysts such as iron oxyhydroxides and manganese oxyhydroxides, as well as transition elements resulting from mineral dissolution. The most common organic catalysts are enzymes, such as catalase and peroxidase, which are produced to detoxify H₂O₂ in the cellular and extracellular environment (Huling et al. 1991). Catalase is the most active of the naturally occurring inorganic and enzymatic catalysts that decompose H₂O₂ (Schumb et al. 1955).

Because H₂O₂ is unstable in soil systems, it may be difficult to apply to the surface of a soil for in-situ remediation without decomposing close to the surface. In the only work of this nature, Ravikumar and Gurol (1994) studied the remediation of contaminated commercial sand in soil columns using catalyzed H₂O₂. However, sorption of the contaminants, pentachlorophenol (PCP) and trichloroethylene (TCE), did not limit contaminant degradation because the oxidation occurred primarily in the aqueous phase. More commonly, contaminants are strongly sorbed to soils and the design of in-situ remediation based on rates of desorption may not be feasible. Sedlak and Andren (1994) reported that sorption significantly affected the transformation rates of polychlorinated biphenyls (PCBs) in a Fenton's system. Furthermore, Sheldon and Kochi (1981) stated that most compounds not present in the aqueous phase (i.e. those found in other phases), are not available for reactions with hydroxyl radicals because the oxidants are generated in the aqueous phase.

Recent studies have shown that aggressive Fenton-like reactions have the potential to oxidize sorbed contaminants. Watts et al. (1994) documented the oxidation of sorbed hexachlorobenzene (log K_{ow} = 6.2), which was degraded more rapidly than it was desorbed with H₂O₂ concentrations greater than 30 mM using soluble iron (II) at H₂O₂:Fe molar ratios of 2:1. They hypothesized that the rapid rates of oxidation were