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The Effect of Citric Acid on the Oxidation of Organic Contaminants by Fenton's Reagent

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Combined with acids and iron catalysts, hydrogen peroxide (H_2O_2) as Fenton's reagent is proven to be effective in oxidizing halogenated volatile organic compounds (VOCs). The Fenton's reagent, traditionally used for waste water treatment, has been applied to the remediation of contaminated soil systems and numerous investigators have found intrinsic iron salts are an effective source of iron catalyst for the reaction. Citric acid, which is a naturally occurring nutrient to microorganisms and less destructive to soil chemical properties, was selected for an acidifying agent to create acidic soil condition. However, citric acid has been considered as a reaction inhibitor because it sequesters ferric iron from Fenton's catalytic cycle by forming strong chelates with iron. This paper presents the feasibility of using citric acid as an acidifying agent of soil matrix for the Fenton-like oxidation.

Series of batch tests were performed to test oxidation of VOCs in various aqueous systems with two acidifying agents (citric acid or sulfuric acid) and three iron sources (iron sulfate, water soluble soil iron, or soil matrix). Batch results show that soluble iron is essential for near complete disappearance of VOCs and that citric acid performs similarly to sulfuric acid at low H_2O_2 dosage (< 1 wt%). The test soil provided water-soluble soil iron but also contained scavengers of the oxidizing agents, resulting in limited removals of VOCs. Column tests confirmed the results of the batch tests, suggesting citric acid is also as effective as sulfuric acid in providing acidic environment for the Fenton-like oxidation.

The batch experiments also reveal that higher doses of H_2O_2 lower the degree of VOC removals in citric acid systems. Potential explanations for this declining include that excessive presence of H_2O_2 expedites the oxidation of ferrous to ferric iron, which then forms a strong complex with citrate, leading to the sequestration of the iron from the Fenton's reaction cycle. Consequently, an additional supply of ferrous iron would be required for continuing oxidation of VOCs, as well as slow injection of H_2O_2 . A detailed mechanistic study would be needed for factual understanding.