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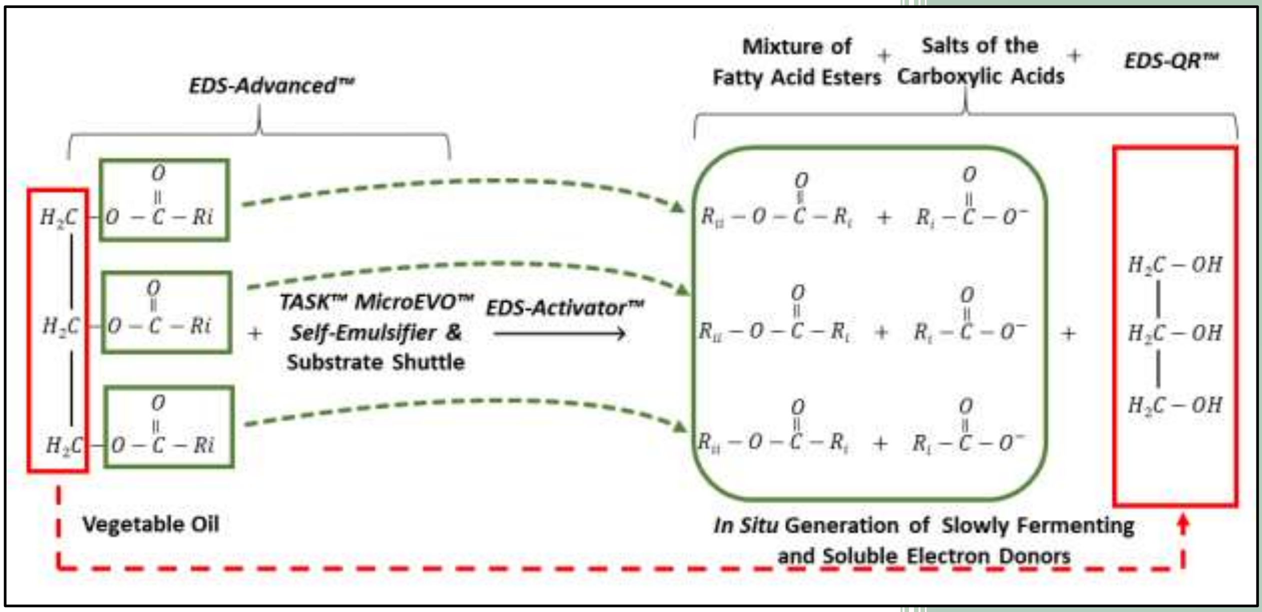
Heat-Enhanced Catalyzed Reductive Bioremediation



Transesterification of vegetable oils, reaction of a triglyceride with a catalyst

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Combination of Thermal Treatment and Microbial Reductive Dechlorination

Background

Heat-enhanced catalyzed reductive bioremediation seamlessly combines the advantages of low-temperature *in-situ* thermal treatment with the effectiveness of reductive bioremediation, effectively addressing challenges such as cost-efficiency in heating contaminated areas and reducing the duration of the cleanup process associated with reductive bioremediation. Our innovative approach overcomes the inherent obstacles of each method, offering a comprehensive solution for efficient and accelerated environmental remediation.

In-situ thermal treatment and *in-situ* reductive dechlorination are valuable methods for addressing chlorinated solvent contamination. However, it is rare to achieve complete contaminant removal using a single technology, as noted in Beyke et al. (2005), Löffler et al. (2013a), and Stroo et al. (2003).

In the United States, most aquifers maintain an average temperature of approximately 15°C. Notably, organohalide-respiring bacteria thrive within a temperature range of 25 to 30°C (Löffler et al., 2013b). Thermally enhanced bioremediation has been successful in combating chlorinated solvent contamination. The application of heat improves the process by reducing dissolved oxygen levels in the aquifer, aiding the release of chlorinated volatile organic compounds from the matrix, and increasing the concentrations of dissolved organic carbon (electron donors). Additionally, the added heat directly stimulates dechlorinating bacteria within their optimal temperature range.

The combination of thermal treatment and microbial reductive dechlorination offers a cost-effective solution for addressing contaminant rebound in groundwater remediation at moderate temperatures. It's important to note that Marcet et al., (2018) reported that at temperatures above 43°C dechlorination activities decrease and minimal biological or chemical destruction of chloroethenes occurs at temperatures above 50°C (Costanza et al., 2009; Stroo et al., 2012).

However, conventional in-situ heating methods (e.g., Electrical Resistance Heating - ERH, Thermal Conduction Heating - TCH) demand substantial subgrade heating equipment, vapor recovery and treatment systems, and temperature and pressure monitoring systems. All of these components must be installed and operational before the system can begin, necessitating a significant investment of labor, time, and capital. Furthermore, non-uniform heating of the subsurface often results in varying thermal signatures, particularly in zones with faster groundwater flow, which may heat more slowly. Consequently, justifying the expenses associated with traditional in-situ heating methods for heat-enhanced reductive bioremediation can be challenging, especially given the narrow effective temperature range.

Additionally, thermally enhanced bioremediation requires an assimilable carbon source. Emulsified vegetable oil (EVO) is a commonly used source because it slowly ferments, acting as an organic carbon and hydrogen source in the subsurface, stimulating organohalide-respiring bacteria that mineralize chlorinated solvents. However, experiences with numerous EVO injection events over the years have shown that EVOs effects are limited to the immediate vicinity of the injection point. Proper distribution of the correct type of fatty acids is crucial for anaerobic reductive dechlorination.

Heat-enhanced catalyzed reductive bioremediation effectively addresses two primary challenges associated with thermally enhanced bioremediation: the cost of heating the target contaminated area and the limited distribution of fatty acids in the subsurface.

Approach

Heat-enhanced catalyzed reductive bioremediation represents an innovative approach to in-situ transesterification of vegetable oils, enhancing the creation and distribution of slowly fermenting, water-soluble electron donors crucial for anaerobic reductive bioremediation in contaminated aquifers. This method accelerates transesterification reactions from months to mere hours by applying heat to the process. Heat not only expedites the reaction rate but also increases the yield of fatty acid alkyl esters and temporarily elevates aquifer temperatures into the optimal range, stimulating organohalide-respiring bacteria that efficiently mineralize chlorinated solvents.

The procedure involves introducing a water-soluble oil solvent mixture along with a catalyst into the target contaminated area, facilitating the following key objectives:

a) The cleavage of fatty acids from the triglyceride molecule, which then binds to the alkyl group (comprised of carbon and hydrogen) of the alcohol to produce fatty acid alkyl esters, carboxylic acids/salts, and glycerol.
b) Enhancing the distribution of fatty acids within the subsurface, providing aquifer buffering, and mitigating issues like biofouling and saponification.

The combination of vegetable oil, emulsifier, and water (or variations thereof) is typically heated to temperatures below the boiling point of the mixture, often remaining below 100°C. Various cost-effective heating options are available for this purpose, including hot water boilers, counter-flow hot water generators, water-tube boilers, shell and tube heating tanks, tanks equipped with electric heating coils, tankless heaters, and hot water injection systems.

After preparing this heated mixture, it is injected into the aquifer along with a catalyst. As the injected fluid, now heated, mingles with the native groundwater, the temperature naturally decreases. Once the temperature stabilizes below 40°C, the next step involves bioaugmenting the aquifer with a natural microbial consortium that contains organohalide-respiring bacteria. This microbial consortium plays a vital role in the subsequent bioremediation process.

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Lessons Learned

Heat-enhanced catalyzed reductive bioremediation proves to be a promising remediation approach that effectively combines the strengths of in-situ thermal treatment with enhanced reductive bioremediation. This innovative method leverages the benefits of both technologies while addressing their respective limitations, particularly in terms of cost-efficiency for heating the contaminated area and the duration of the cleanup process.

The injection of heated amendments and water significantly enhances the growth of organohalide-respiring bacteria, leading to increased chlorinated solvent degradation rates. Key monitoring tools, including volatile fatty acids (VFAs), next-generation sequencing (NGS), and compound-specific isotope analysis (CSIA), play crucial roles in evaluating the performance of this approach. VFAs are instrumental in assessing the effectiveness of low-temperature thermal processes, aiding in the solubilization of soil organic matter and the chemical (i.e., transesterification) and biological (i.e., fermentation) breakdown of the electron donor (i.e., EVO). NGS is employed to investigate the impact of heated fluid injection on the microbial community, offering insights into shifts in bacterial populations. CSIA, a powerful analytical tool, provides valuable information that goes beyond what can be obtained from concentration data alone, revealing degradation rates and processes.

Extensive fieldwork has yielded compelling evidence of the technology's effectiveness, showcasing its potential to reduce contaminant mass by up to 90% within just 90 days post-injection. Beyond this initial 90-day period, the slowly fermenting electron donors continue to supply organic carbon and hydrogen, ensuring the sustained stimulation of organohalide-respiring bacteria for the ongoing mineralization of remaining chlorinated solvents.

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