Simultaneous Degradation of Commingled Contaminants by a Microbially-Driven Fenton Reaction Operated in Fed-Batch and Flow-Through Reactor Configurations

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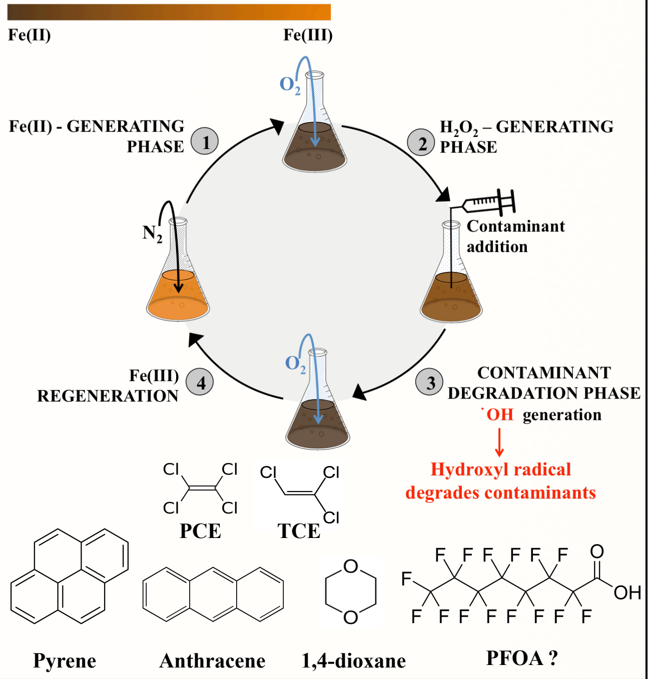
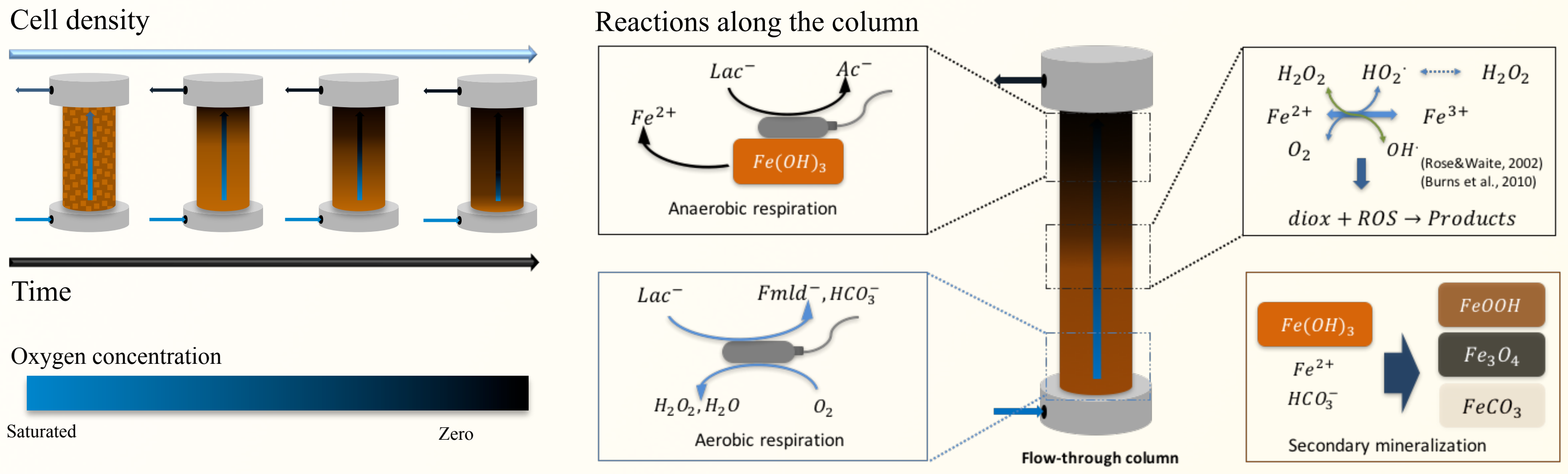
Introduction

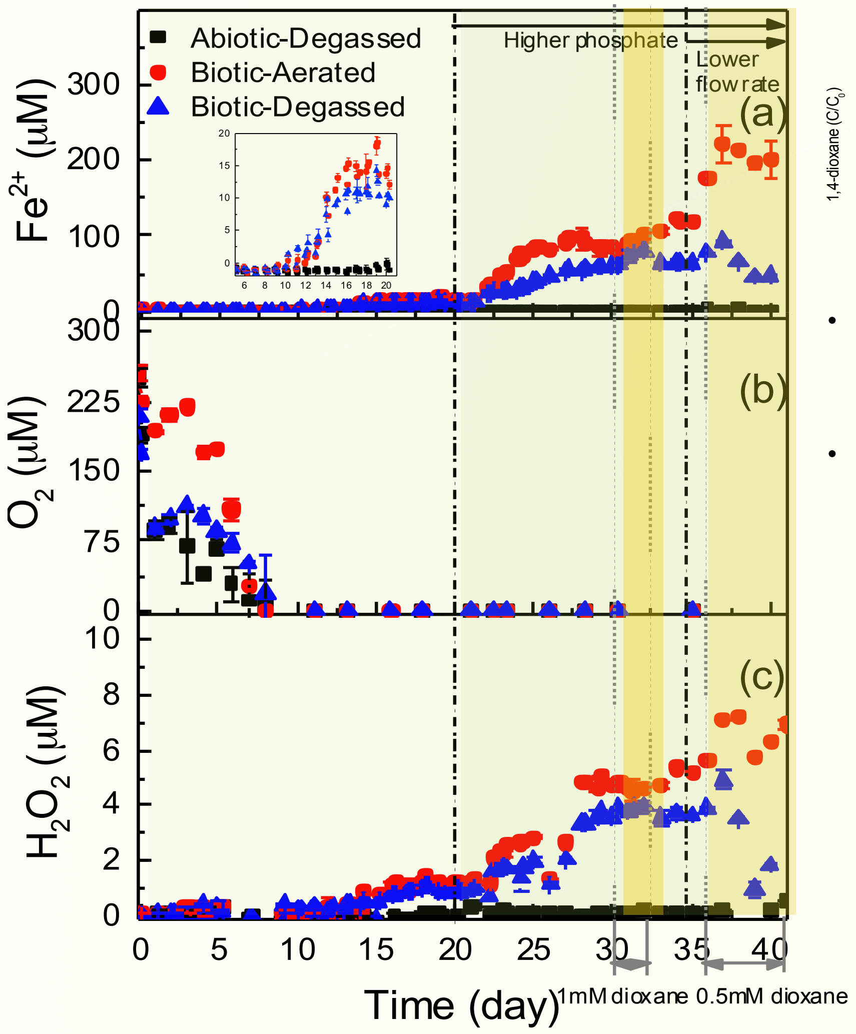
In recent studies, a microbially-driven Fenton reaction system was designed in batch reactors with the Fe(III)-reducing facultative anaerobe *Shewanella oneidensis* to produce H_2O_2 via microbial respiration under aerobic conditions and Fe(II) via microbial Fe(III) reduction under anaerobic conditions. The Fenton reaction promoted by alternating between aerobic and anaerobic conditions generated ROS to degrade source zone levels of TCE, PCE, and 1,4-dioxane as single contaminants or as binary and ternary mixtures. In comparison to conventional (purely abiotic) Fenton reactions, the microbially-driven Fenton reaction operates at circumneutral pH and does not require addition of exogenous H_2O_2 or UV irradiation to regenerate Fe(II). As iron oxyhydroxides and iron-reducing bacteria are ubiquitous in soils and sediments, the microbially-driven Fenton reaction may represent an economical in situ bioremediation strategy for organic contaminants. To sustain the microbially-driven Fenton reaction in the field, however, it is imperative to determine whether redox conditions have to be oscillated over time. In this study, the microbially-driven Fenton reaction for degradation of 1,4-dioxane was reconfigured in flow-through columns loaded with ferrihydrite-coated sand and *S. oneidensis* to mimic typical subsurface conditions. The degradation of PFOA is also being investigated in a batch reactor system, and optimization of PFOA extraction from iron-rich media for LC-MS/MS analyses is a current research focus, as published PFOA extraction protocols traditionally focus on detection of sub nano- or picomolar concentrations from relatively pure solutions.

Fenton reaction: $Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^- + HO^\cdot$

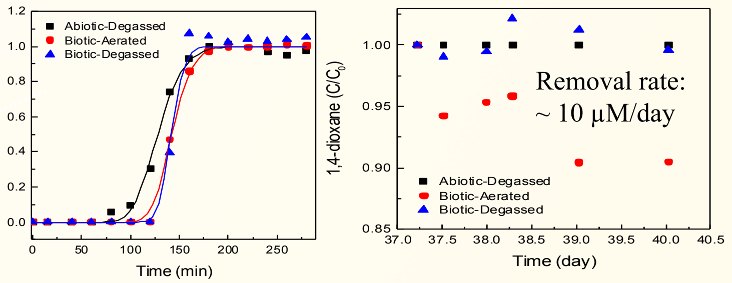


Methods and results: The microbially-driven Fenton reaction at work in a flow-through reactor column with *S. oneidensis*

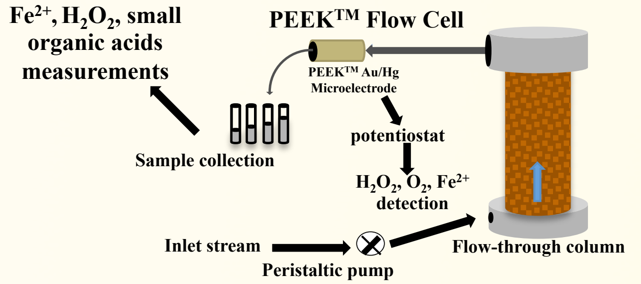




1,4-dioxane concentration in effluent during days 37 – 40



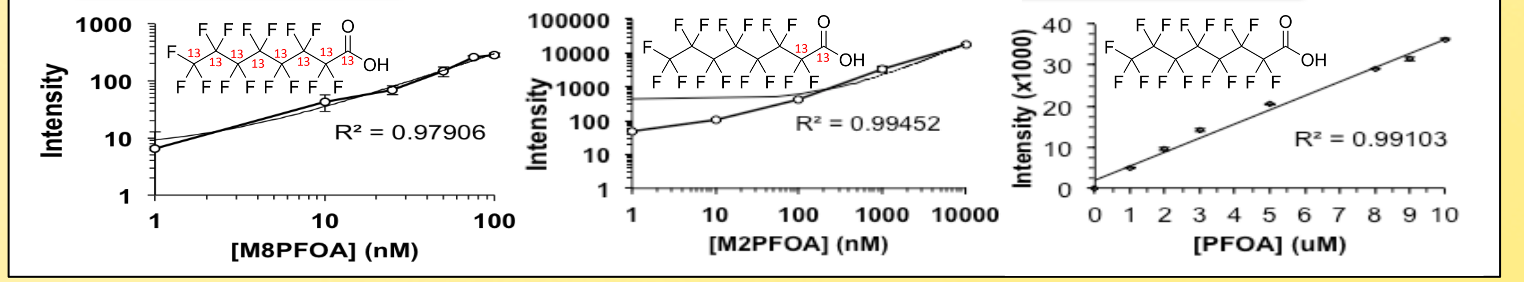
- **The most efficient ROS production is obtained under aerobic conditions, with microbial O_2 consumption resulting in suboxic conditions, simultaneous H_2O_2 and Fe(II) production and evidence of dioxane degradation**
- Current work is focused on column optimization
  - The flow rate may be too high for ROS to completely react with contaminants
  - Would addition of humic acids or AQDS help promote ROS production and mimic a more accurate subsurface environment?



Flow through reactors were amended with two-line ferrihydrite-coated sand, 10^8 S. oneidensis cells/mL, 3mM dioxane.

Method development: Can the microbially-driven Fenton reaction degrade PFOA?

Batch reactor with *S. oneidensis* MR-1, amended with PFOA → Amendment with isotope-labeled PFOA as internal standard → 3x liquid-liquid extraction with methyl *tert*-butyl ether → Liquid chromatography (ACN/H_2O gradient, 5mM amm. ac.) → Tandem mass spectrometry (ESI$^-$) → Data analysis



Conclusions

- In contrast to the purely abiotic chemical Fenton reaction, addition of exogenous H_2O_2 is not required to drive the microbially-driven Fenton reaction, and maintaining low pH conditions is unnecessary
- Our flow-through reactor system may be efficient at degrading chlorinated and other recalcitrant compounds that are resistant to normal enzymatic attack
- **Optimal suboxic conditions may be produced by (1) Feeding aerobic lactate inlet streams with varying lactate concentrations, or (2) Varying aerobic inlet flow rates at constant lactate concentrations**
- The microbially-driven Fenton reaction provides a foundation for development of alternative *in situ* remediation technologies for degradation of recalcitrant compounds in contaminated marine and freshwater environments, as well as contaminated groundwater and sediment

Future directions

- Further manipulation and optimization of environmental conditions in the flow-through reactor system to mimic a more natural subsurface environment for microbial degradation of contaminants
- The microbially-driven Fenton reaction may be induced *in situ* by exposing Fe(III)-reducing facultative anaerobes in Fe(III)-containing contaminated environments to alternating aerobic and anaerobic conditions via alternating injections of compressed air and nitrogen.
- Degradation of other recalcitrant compounds including perfluoroalkyl substances (PFAS) in batch, fed-batch and flow-through reactor systems

Acknowledgements

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