Colorado State University

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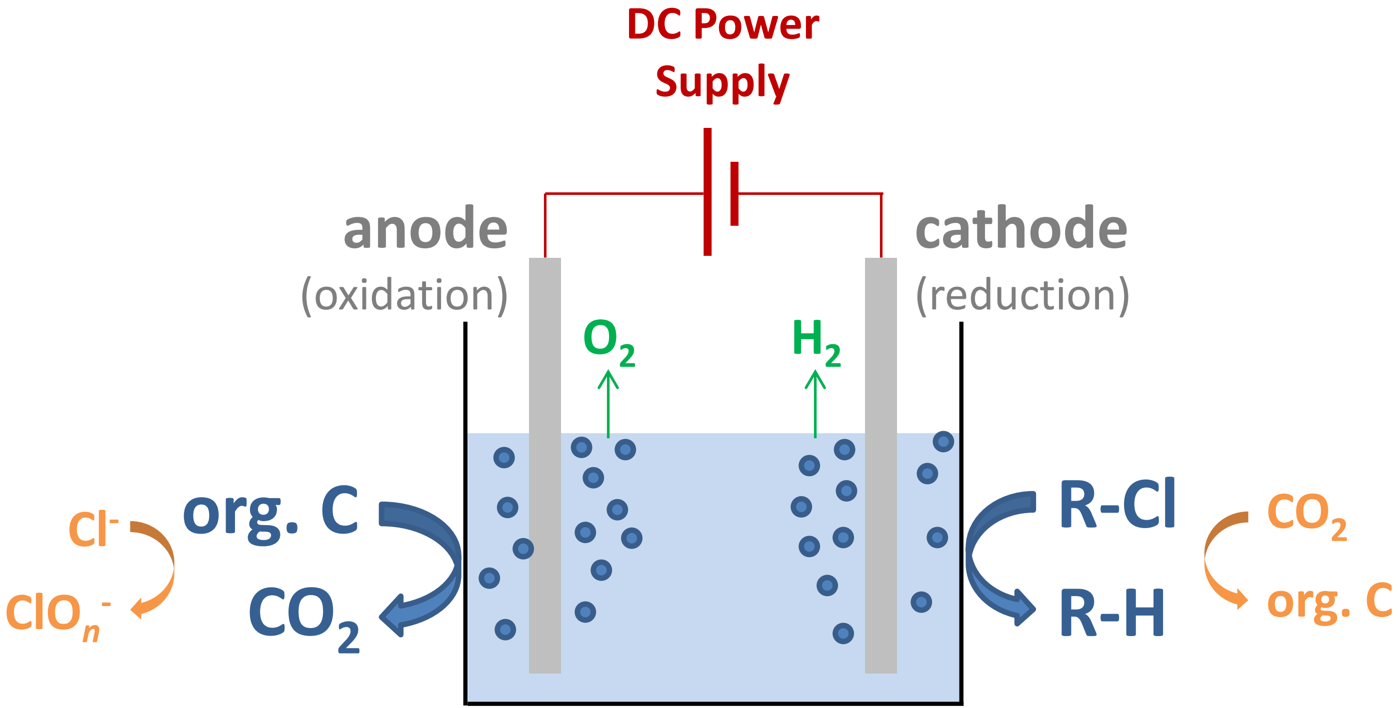
Current Advances in Bioelectrochemical Treatment of Persistent Groundwater Contaminants

Jens Blotevogel[1], Shaily Mahendra[2]

[1]Colorado State University, Fort Collins, CO

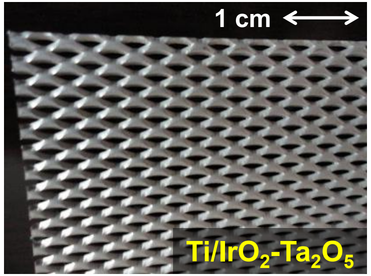
[2]University of California, Los Angeles, CA

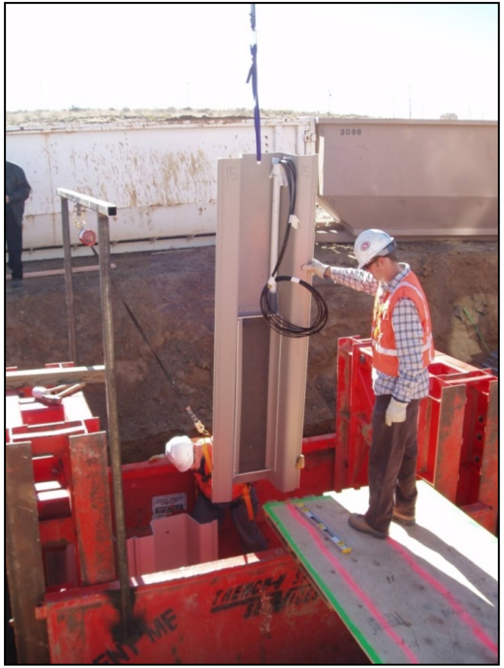
Electrochemical water treatment can degrade virtually any organic contaminant.



$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4e^-$ $\quad$ $2\ H^+ + 2e^- \rightarrow H_2$

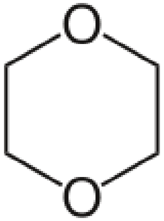
Field installation of mesh electrodes as permeable reactive barrier (e^-barrier)





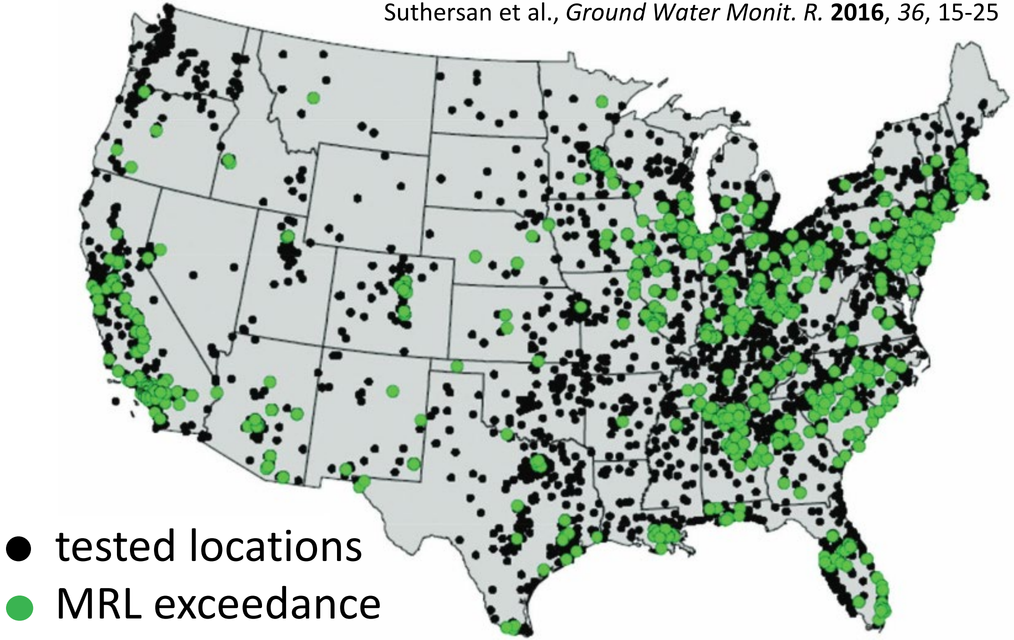
Blotevogel, J.: An electric fix for removing longlasting chemicals in groundwater. *The Conversation*, 04/10/2017

1,4-Dioxane is one of the most widely detected organic compounds in U.S. water wells.



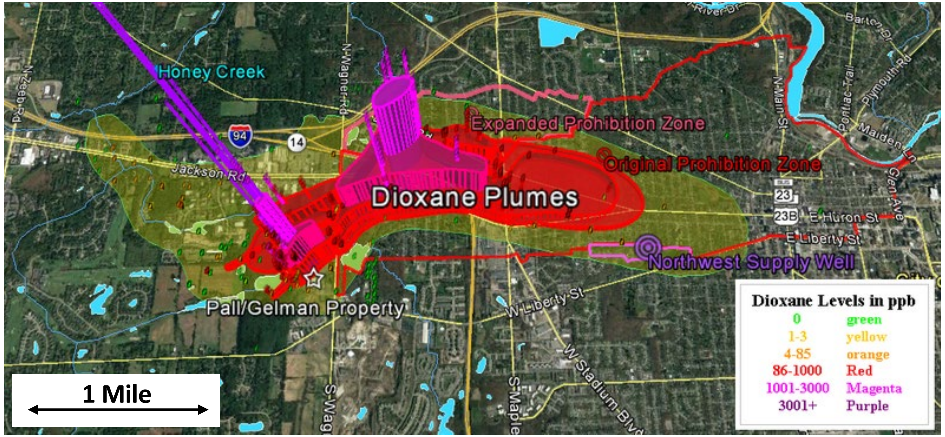
liver & kidney toxicity, probable human carcinogen (U.S.EPA)

Suthersan et al., *Ground Water Monit. R.* **2016**, *36*, 15-25



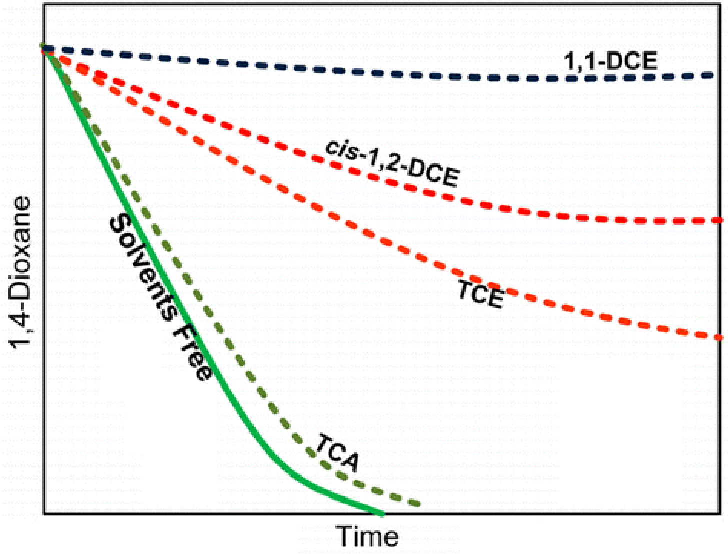
U.S. EPA Health Guideline 0.35 µg/L

1,4-Dioxane is highly mobile and its biodegradation inhibited by chlorinated solvents.

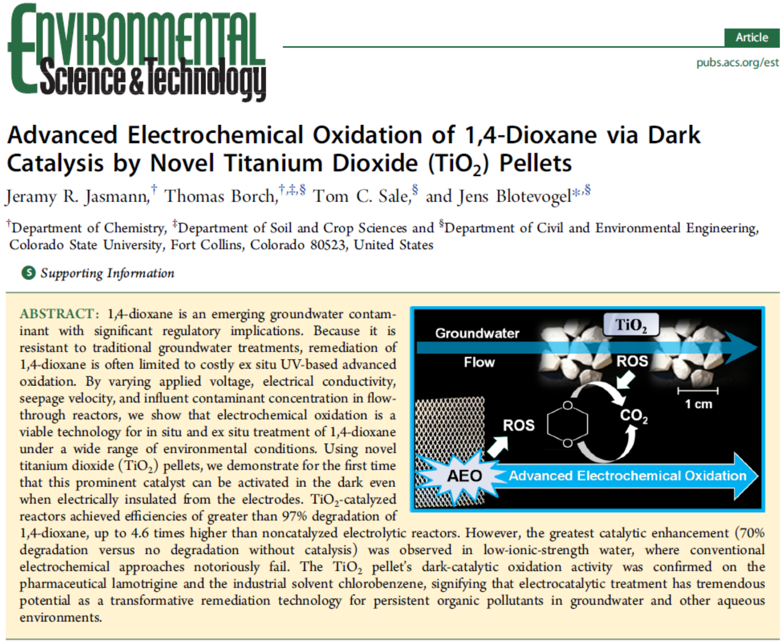


Source: National Public Radio 2018

Zhang, S.; **Mahendra, S.** et al., *Environ.Sci.Technol.* **2016**, *50*, 9599



Electrochemical treatment oxidizes 1,4-dioxane, but energy efficiency is low.


Environmental Science & Technology

Article

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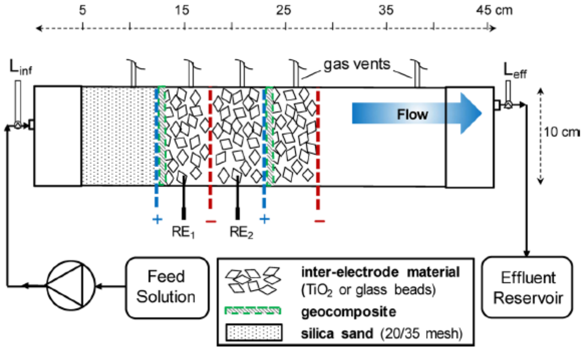
Advanced Electrochemical Oxidation of 1,4-Dioxane via Dark Catalysis by Novel Titanium Dioxide (TiO_2) Pellets

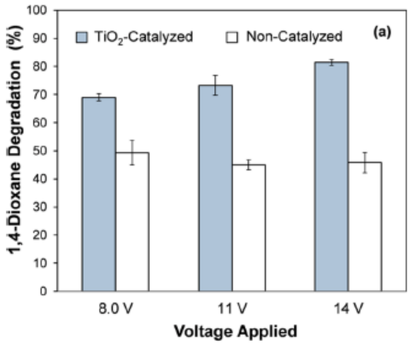
Jeramy R. Jasmann,[†] Thomas Borch,[†,‡,§] Tom C. Sale,[§] and Jens Blotevogel*[,§]

[†]Department of Chemistry, [‡]Department of Soil and Crop Sciences and [§]Department of Civil and Environmental Engineering, Colorado State University, Fort Collins, Colorado 80523, United States

Supporting Information

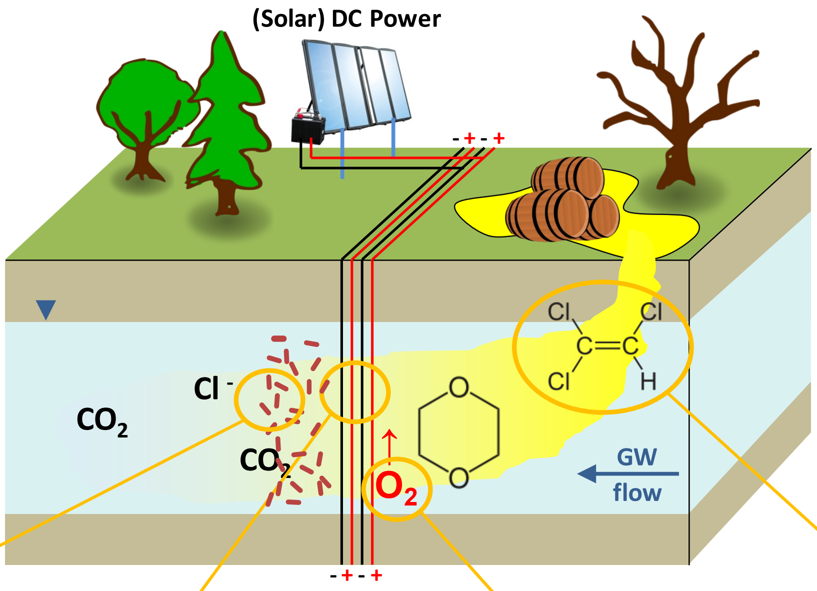
ABSTRACT: 1,4-dioxane is an emerging groundwater contaminant with significant regulatory implications. Because it is resistant to traditional groundwater treatments, remediation of 1,4-dioxane is often limited to costly ex situ UV-based advanced oxidation. By varying applied voltage, electrical conductivity, seepage velocity, and influent contaminant concentration in flow-through reactors, we show that electrochemical oxidation is a viable technology for in situ and ex situ treatment of 1,4-dioxane under a wide range of environmental conditions. Using novel titanium dioxide (TiO_2) pellets, we demonstrate for the first time that this prominent catalyst can be activated in the dark even when electrically insulated from the electrodes. TiO_2-catalyzed reactors achieved efficiencies of greater than 97% degradation of 1,4-dioxane, up to 4.6 times higher than noncatalyzed electrolytic reactors. However, the greatest catalytic enhancement (70% degradation versus no degradation without catalysis) was observed in low-ionic-strength water, where conventional electrochemical approaches notoriously fail. The TiO_2 pellet's dark-catalytic oxidation activity was confirmed on the pharmaceutical lamotrigine and the industrial solvent chlorobenzene, signifying that electrocatalytic treatment has tremendous potential as a transformative remediation technology for persistent organic pollutants in groundwater and other aqueous environments.





Faradaic Efficiency < 99.99%

Conceptual model for bioelectrochemical treatment: harnessing synergistic effects.



biodegradation downstream in milder conditions

direct anodic oxidation of 1,4-dioxane

e^--acceptor for aerobic 1,4-D biodegradation

electrolytic degradation of inhibiting co-contaminants

Pseudonocardia dioxanivorans CB1190 can aerobically metabolize 1,4-dioxane.

Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. 2017, 51, 12619-12629

pubs.acs.org/est

Synergistic Treatment of Mixed 1,4-Dioxane and Chlorinated Solvent Contaminations by Coupling Electrochemical Oxidation with Aerobic Biodegradation

Jeramy R. Jasmann,[†,⊥] Phillip B. Gedalanga,[‡] Thomas Borch,[†,§,∥] Shaily Mahendra,[‡] and Jens Blotevogel[*,§]

[†]Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, United States

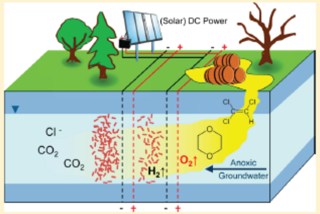
[‡]Department of Civil and Environmental Engineering, University of California, Los Angeles, California 90095, United States

[§]Department of Civil and Environmental Engineering, Colorado State University, Fort Collins, Colorado 80523, United States

[∥]Department of Soil and Crop Sciences, Colorado State University, Fort Collins, Colorado 80523, United States

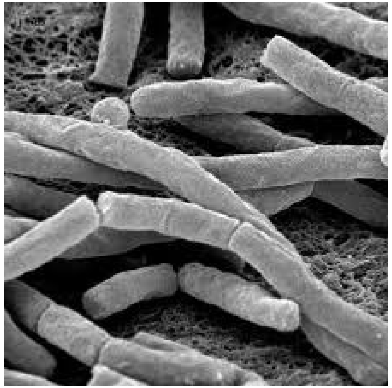
Supporting Information

ABSTRACT: Biodegradation of the persistent groundwater contaminant 1,4-dioxane is often hindered by the absence of dissolved oxygen and the co-occurrence of inhibiting chlorinated solvents. Using flow-through electrolytic reactors equipped with Ti/IrO_2–Ta_2O_5 mesh electrodes, we show that combining electrochemical oxidation with aerobic biodegradation produces an overadditive treatment effect for degrading 1,4-dioxane. In reactors bioaugmented by *Pseudonocardia dioxanivorans* CB1190 with 3.0 V applied, 1,4-dioxane was oxidized 2.5 times faster than in bioaugmented control reactors without an applied potential, and 12 times faster than by abiotic electrolysis only. Quantitative polymerase chain reaction analyses of CB1190 abundance, oxidation−reduction potential, and dissolved oxygen measurements indicated that microbial growth was promoted by anodic oxygen-generating reactions. At a higher potential of 8.0 V, however, the cell abundance near the anode was diminished, likely due to unfavorable pH and/or redox conditions. When coupled to electrolysis, biodegradation of 1,4-dioxane was sustained even in the presence of the common co-contaminant trichloroethene in the influent. Our findings demonstrate that combining electrolytic treatment with aerobic biodegradation may be a promising synergistic approach for the treatment of mixed contaminants.



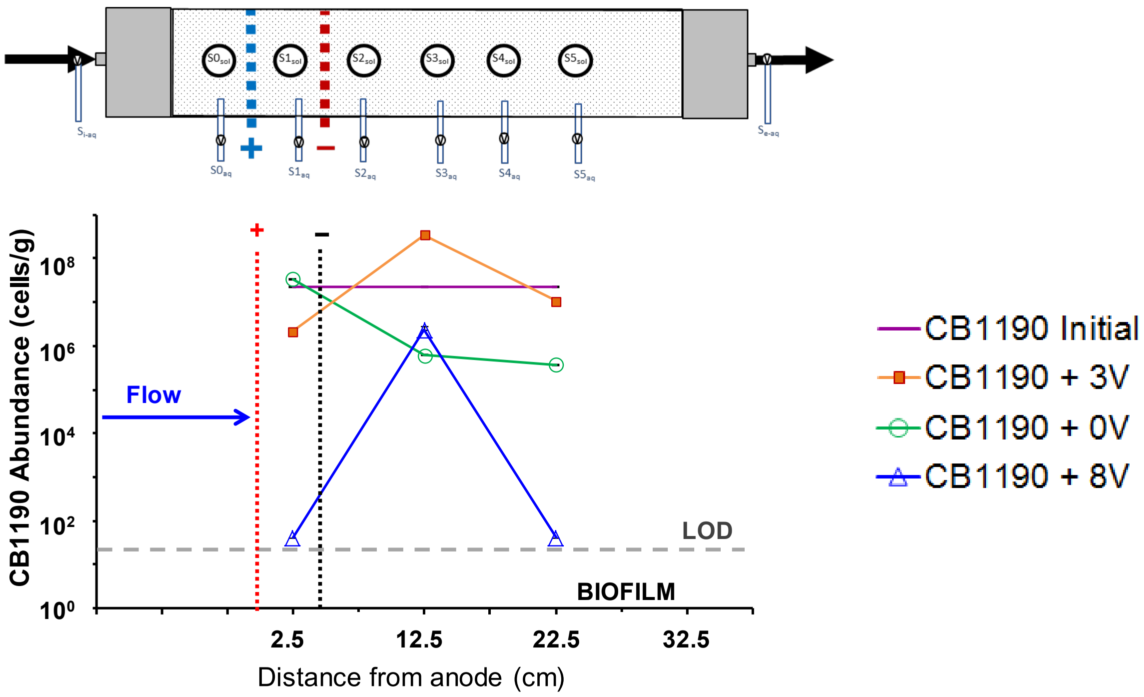
***Pseudonocardia dioxanivorans* CB1190**

- grows using 1,4-dioxane as the sole source of carbon and energy
- monooxygenase initiates ether bond cleavage
- 1,4-dioxane is completely mineralized to CO_2
- biodegradation is inhibited by CVOCs
  1,1-DCE > *cis*-1,2-DCE > TCE > 1,1,1-TCA

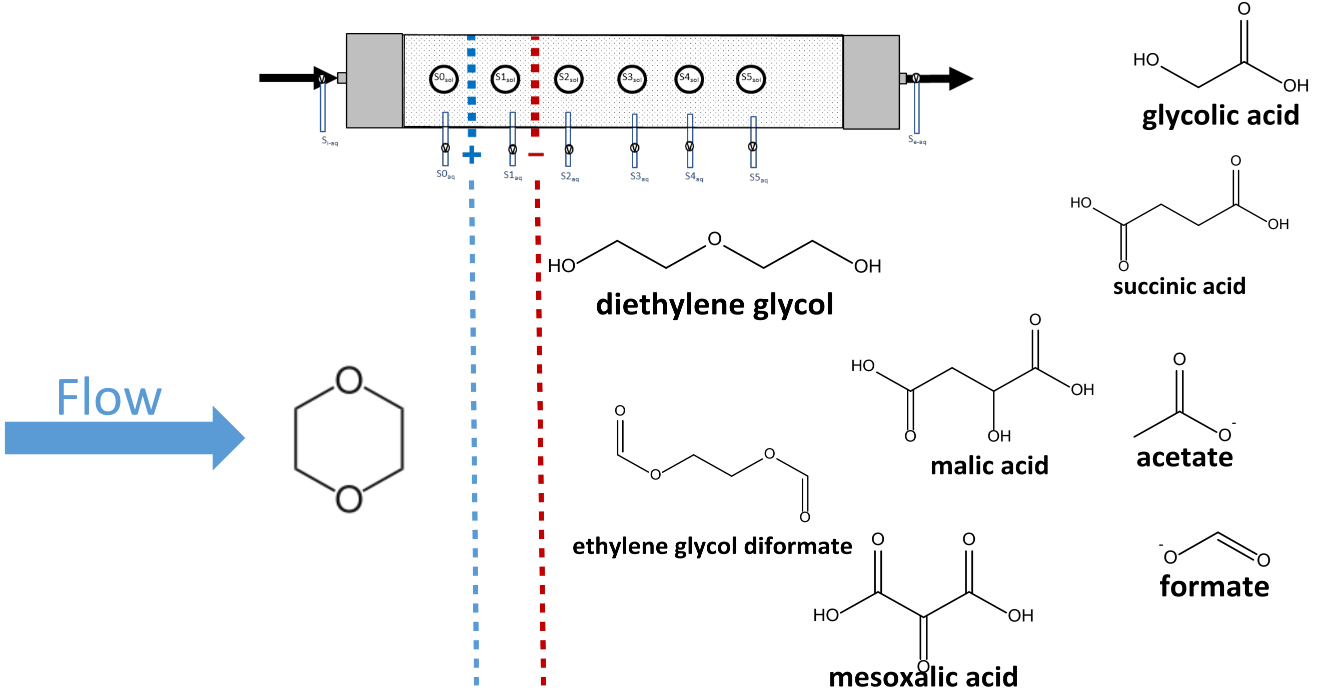


Mahendra, S. & Alvarez-Cohen, L. 2005, 2006, 2007, 2013. Zhang, S.; Gedalanga, P.B.; **Mahendra, S.** 2016, 2017

qPCR reveals “sweet spot” of bacterial abundance ~10-15 cm downstream of anode.

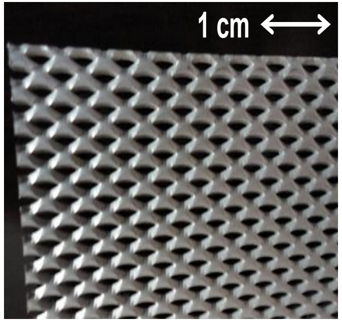


Incomplete electrochemical 1,4-dioxane oxidation generates growth-supporting intermediates.

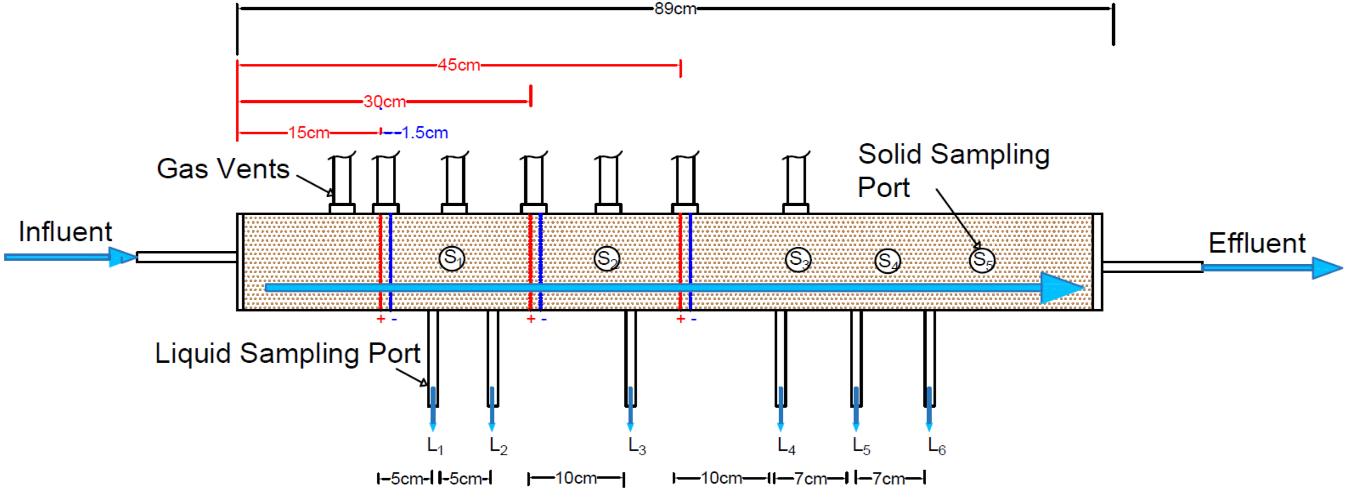


Jasmann, J.R.; **Blotevogel, J.** et al., *Environmental Science & Technology* **2016**, *50*, 8817-8826
Jasmann, J.R.; **Blotevogel, J.** et al., *Environmental Science & Technology* **2017**, *51*, 12619-12629
Blotevogel, J. et al., *Ground Water Monit. R.* **2019**, *39*, 36-42

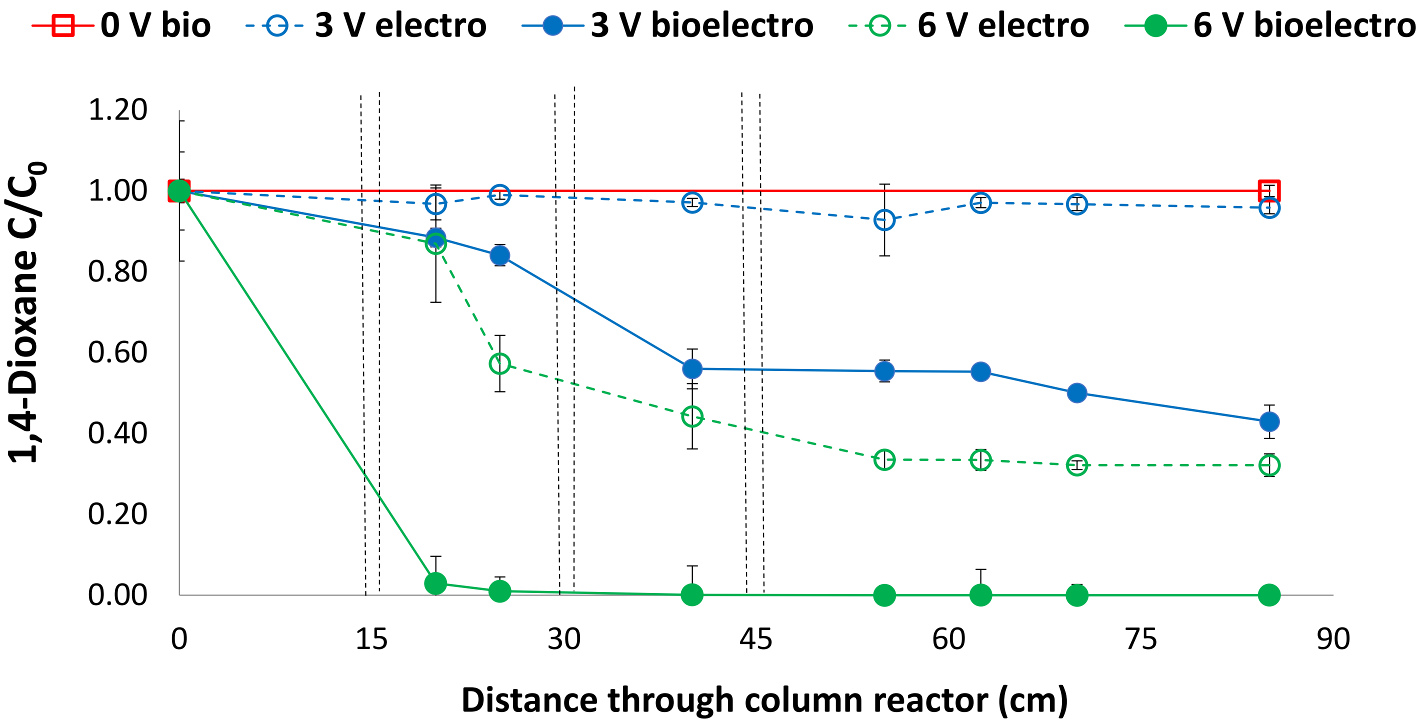
Design of a 2nd generation bioelectrochemical reactor



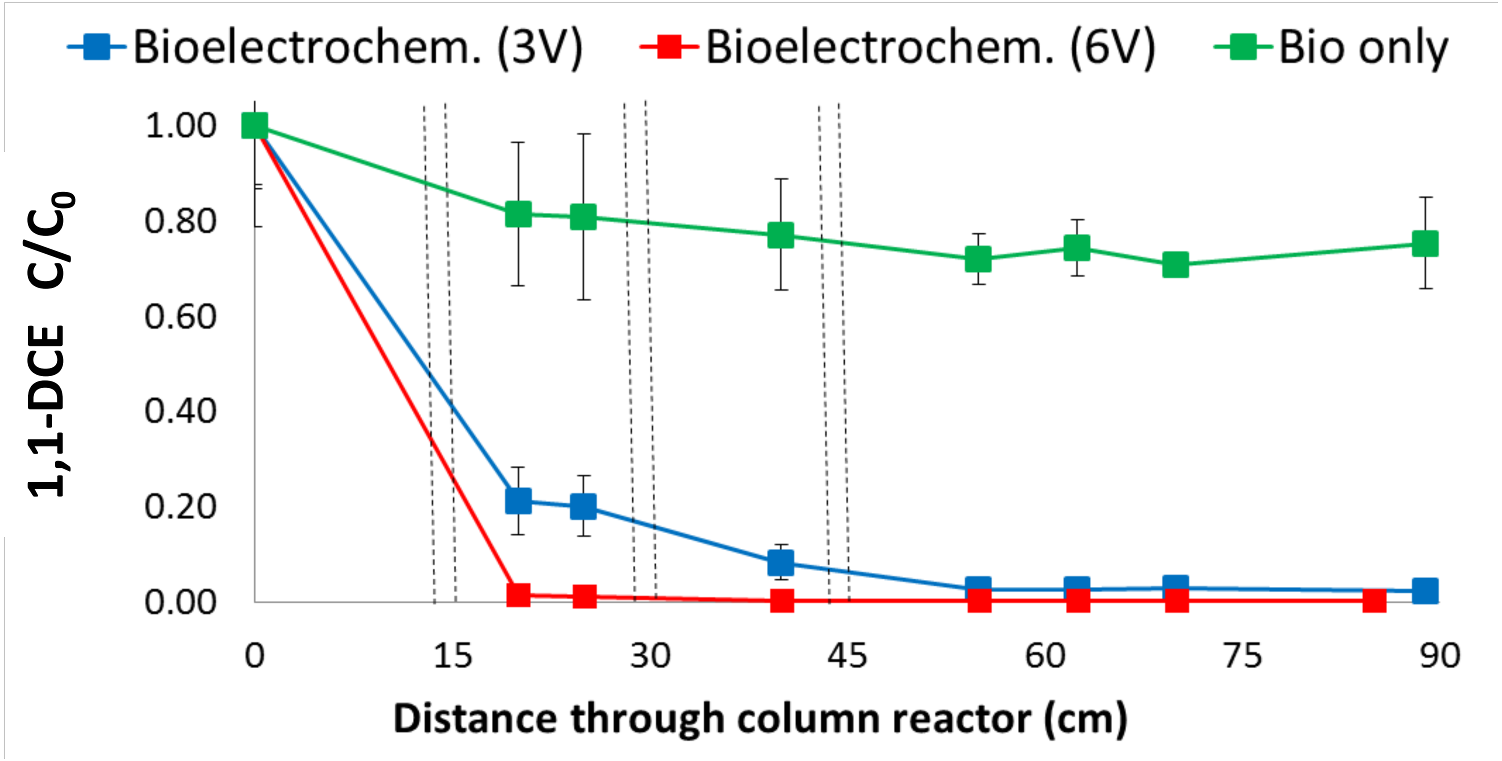
Ti/SnO_2-X mesh anodes



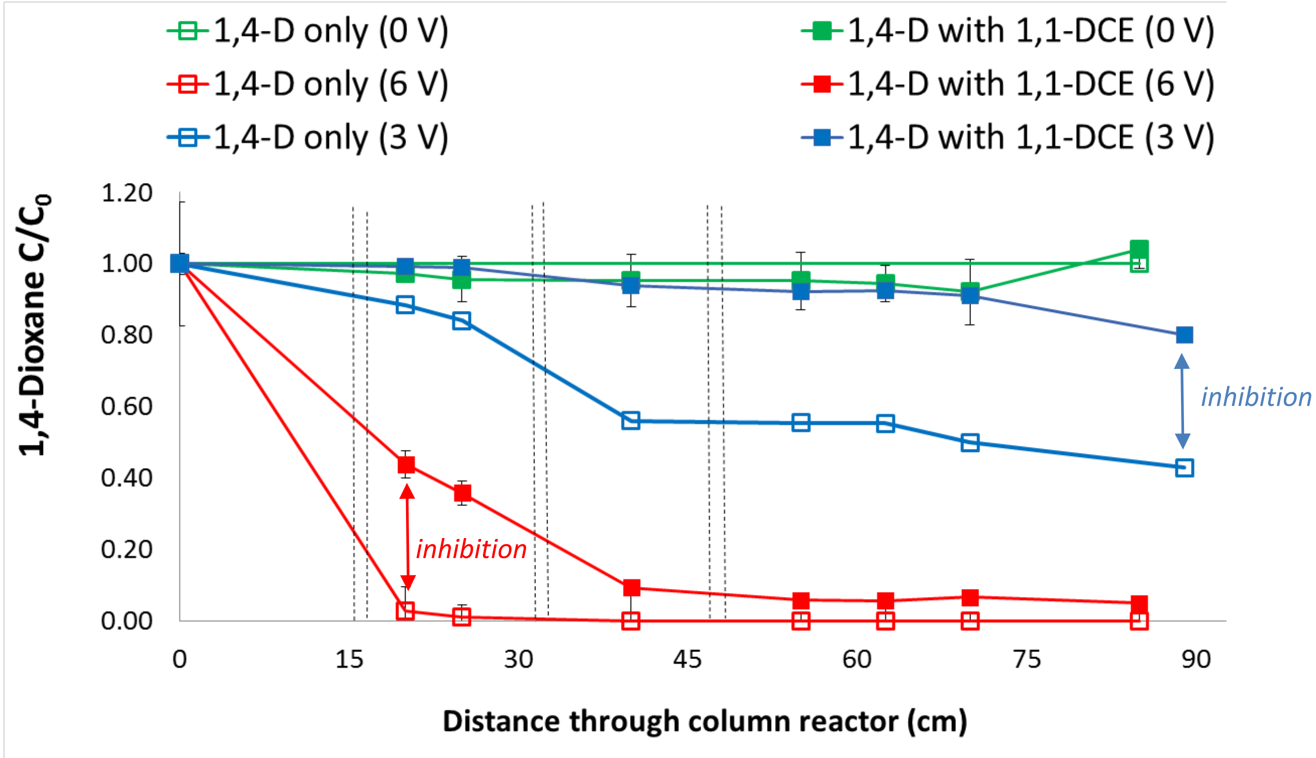
Bioelectrochemical treatment decreased 1,4-dioxane from >100,000 to < 3 µg/L.



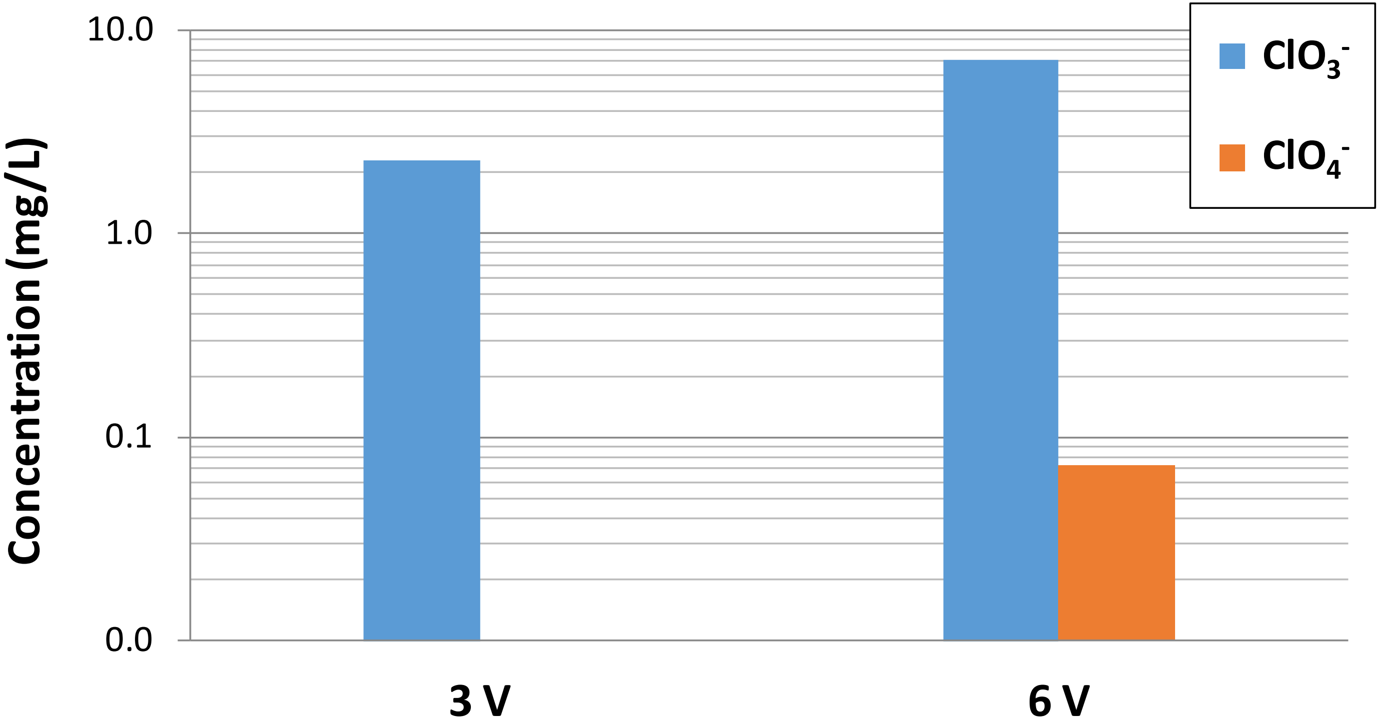
The common co-contaminant and inhibitor 1,1-DCE is removed by 99 %.



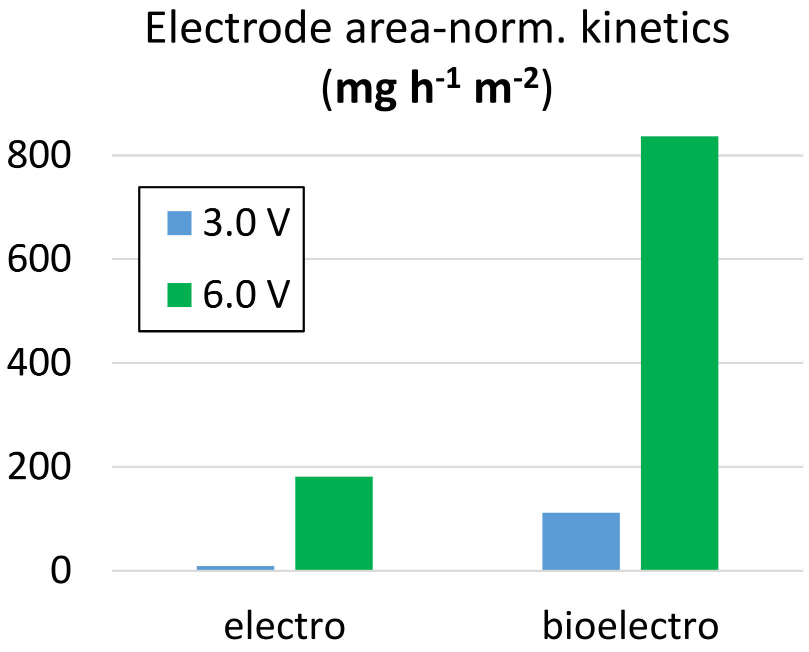
Despite ~99 % 1,1-DCE removal, 1,4-dioxane biodegradation is still slowed.

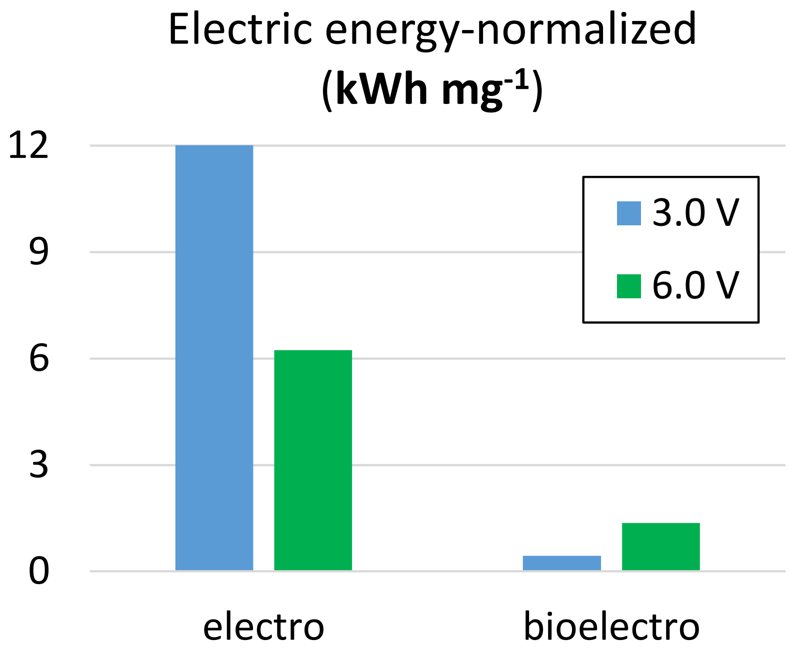


Less oxidation by-products are formed at lower applied potential.

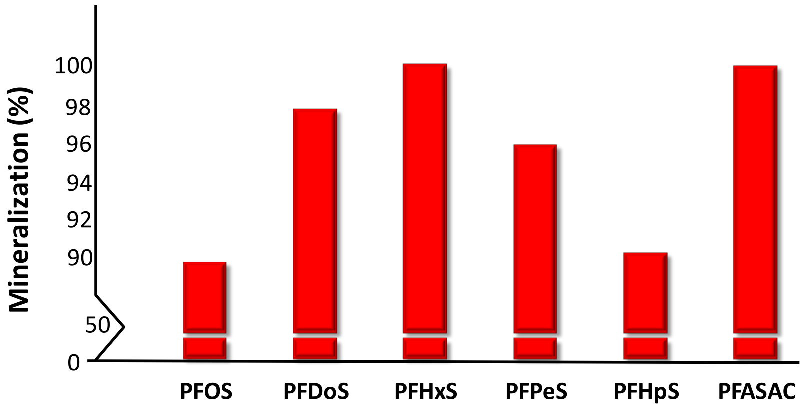


Bioelectrochemical treatment of 1,4-D has lower material usage and energy consumption.

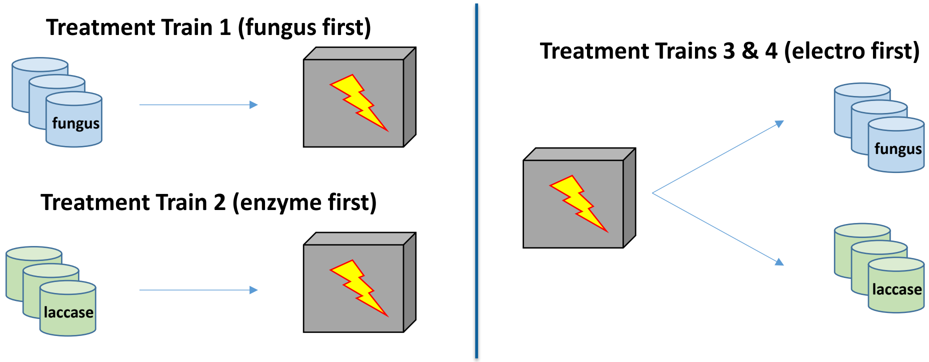




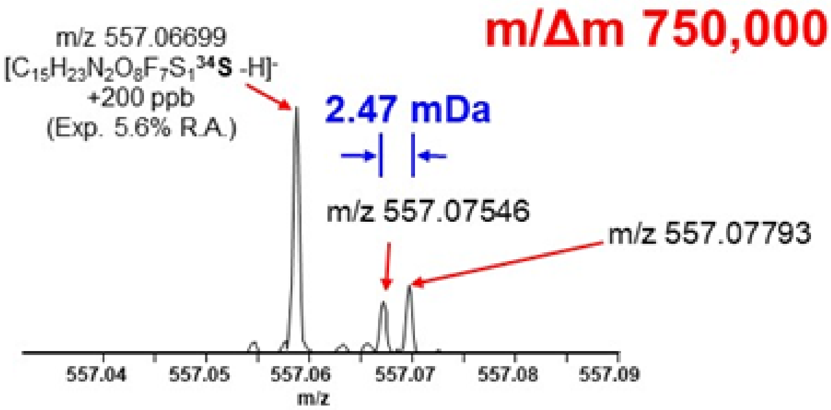
Electrochemical oxidation mineralizes PFASs in AFFFs, but can biological processes help?



6-hour electrochemical oxidation at a boron-doped diamond anode (BDD)

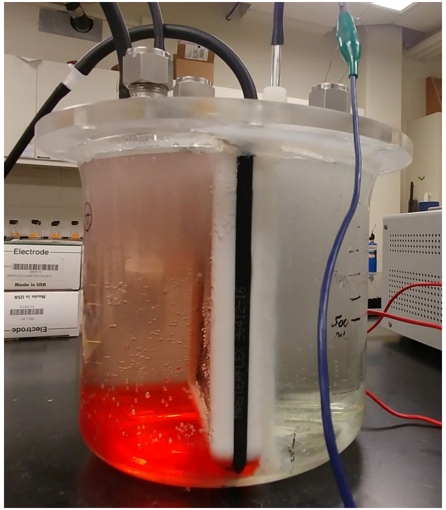


Ultrahigh-resolution mass spectrometry unravels composition of complex AFFF mixtures



Fourier-**T**ransform **I**on **C**yclotron **R**esonance (**FTICR**) mass spectrometry detects ~20,000 compounds in AFFF.

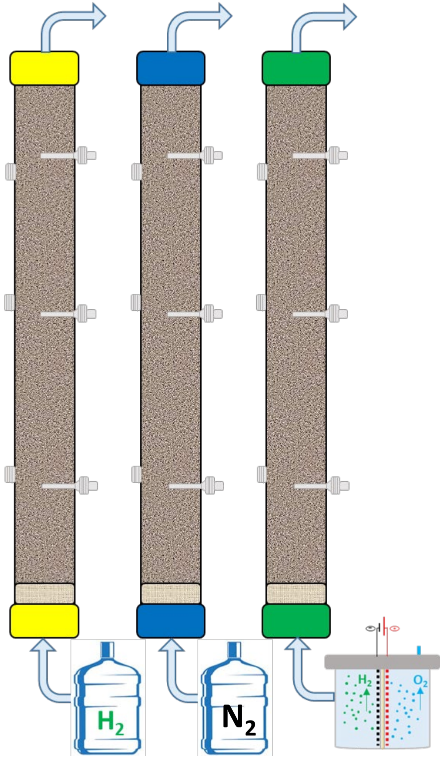
Current development of bioelectrochemical reduction for perchlorate-contaminated groundwater

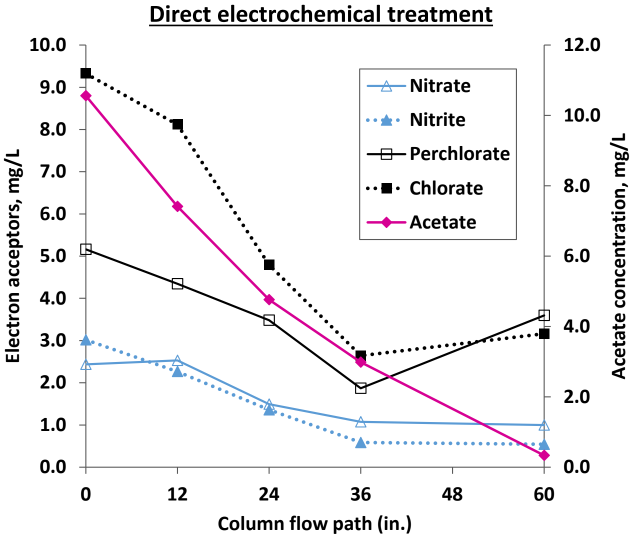


CATHODIC REDUCTION

$H^+ \rightarrow H_2$

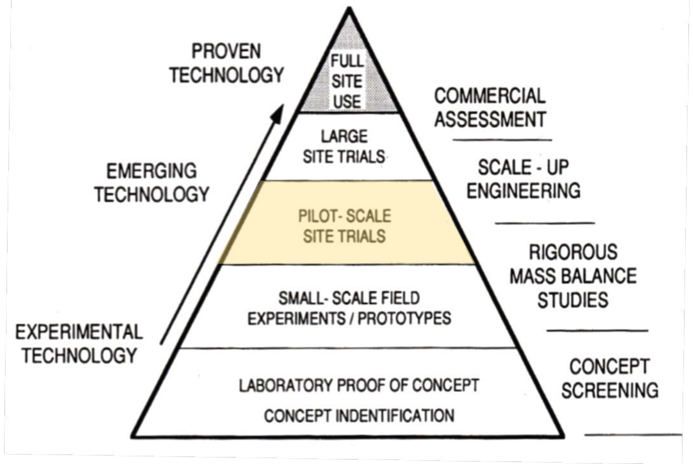
$CO_2 \rightarrow$ acetate

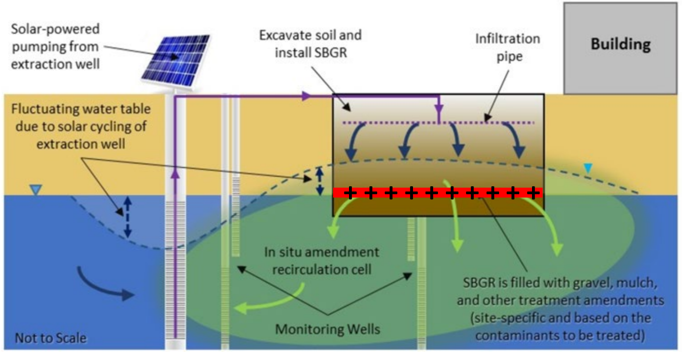




Scaling up bioelectrochemical treatment

Pankow & Cherry 1996





Electrobiogeochemical reactor (e$^-$BGR)

modified from Gamlin & Downey, Enviro Wiki

Blotevogel, J. et al., *Ground Water Monit. R.* **2019**, *39*, 36-42

Summary – benefits of bioelectrochemical treatment

- **synergistic treatment effects:**
  - microbial utilization of O_2 and H_2
  - transformation of persistent parent compounds into growth-supporting intermediates
  - removal of inhibiting co-contaminants
- **reduced electrode material usage**
- **increased electrode service life**
- **lower energy consumption**
- **decreased by-product formation**

Acknowledgements

Colorado State University

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