Perchlorate Degradation in Hydrogen-fed (Autotrophic) Bioreactors

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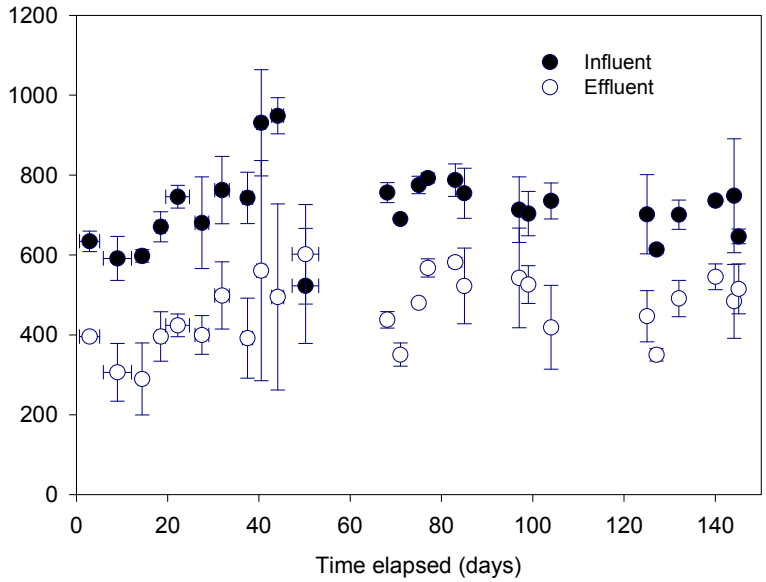
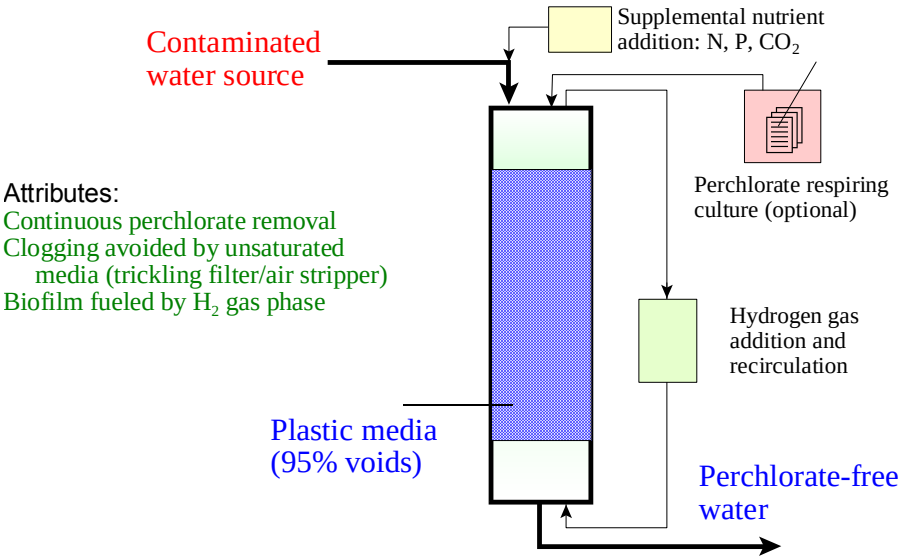


Attributes:
Continuous perchlorate removal
Clogging avoided by unsaturated media (trickling filter/air stripper)
Biofilm fueled by H_2 gas phase



Hydrogen-oxidizing, autotrophic, perchlorate reduction is possible

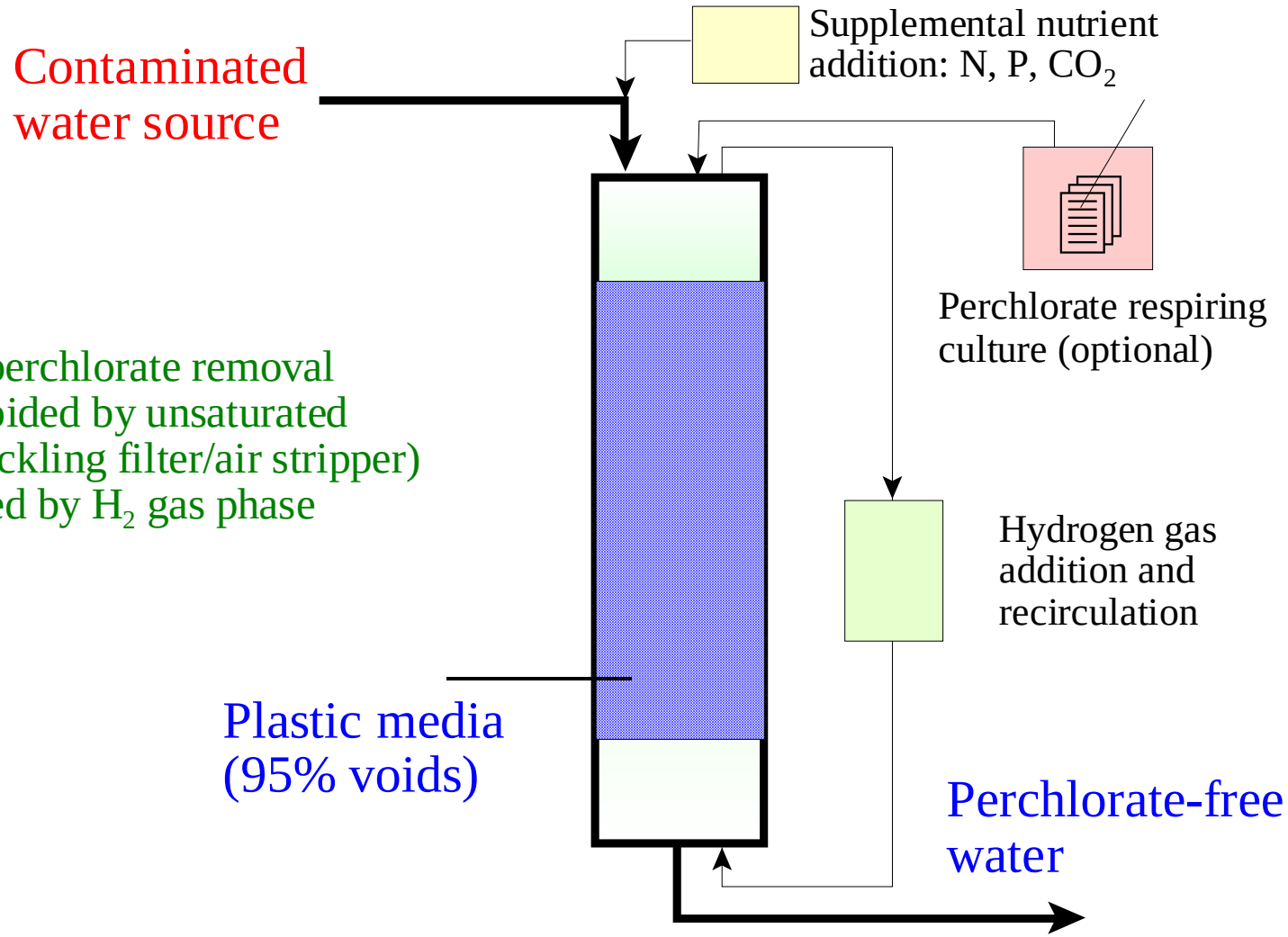
$$H_2 + \frac{1}{4}ClO_4^- \rightarrow \frac{1}{4}Cl^- + H_2O$$

- Rockets are propelled by hydrogen, and (ammonium) perchlorate serves as the oxidizer.
- Biological perchlorate reduction using hydrogen seemed feasible (thermodynamically favorable)
- Needed to have an autotrophic (using inorganic CO_2) microorganism.

Perchlorate Degradation: Topics

- Perchlorate reduction in a fixed bed bioreactor
  - 1: Proof of concept
  - 2: Redesign of reactor, and examination of:
    - Effect of influent perchlorate concentration
    - Alternate electron acceptors
- Comparison of rates in different fixed bed bioreactors: organic versus inorganic (H_2) feeds
- Isolation of an autotrophic, hydrogen-oxidizing, perchlorate-respiring bacterium (*Dechloromonas* sp. HZ)

PSU-O4 Process Patent: Perchlorate degradation in a hydrogen gas fixed bed bioreactor (U.S. Pat. No. 6214607)



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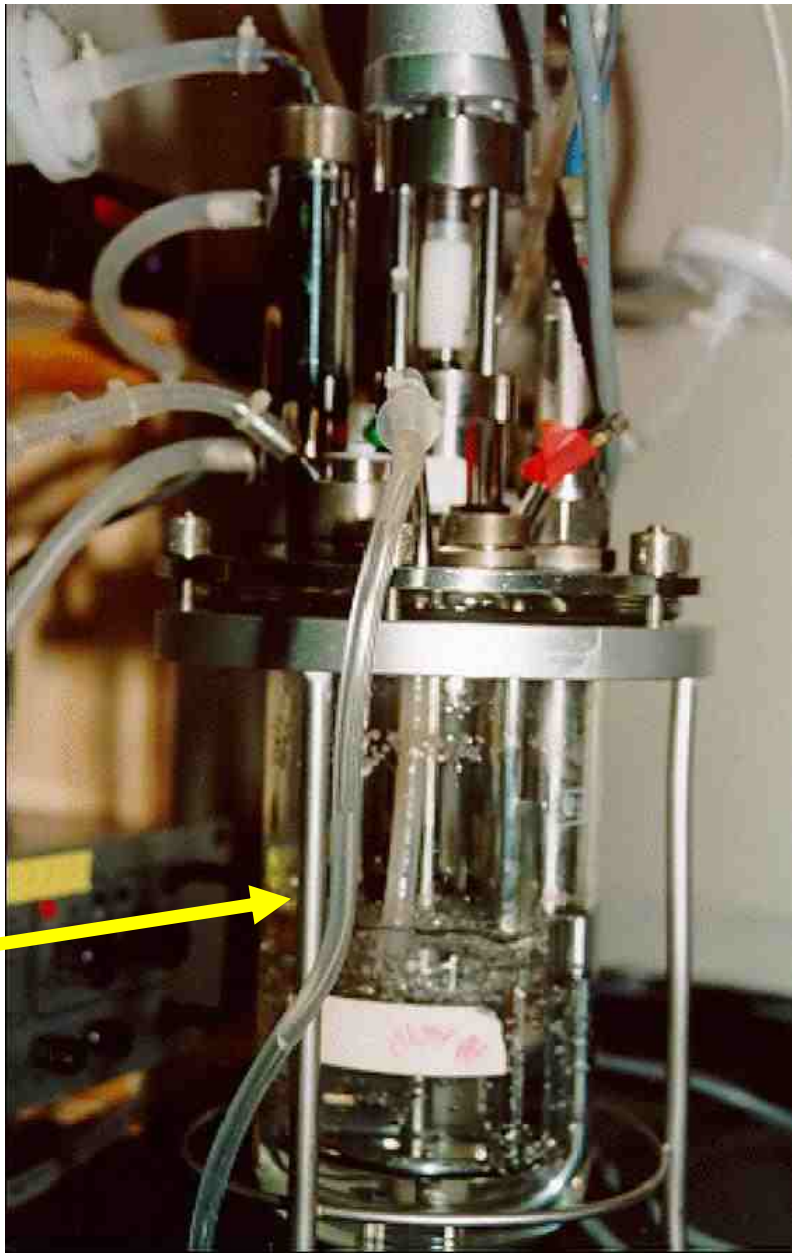
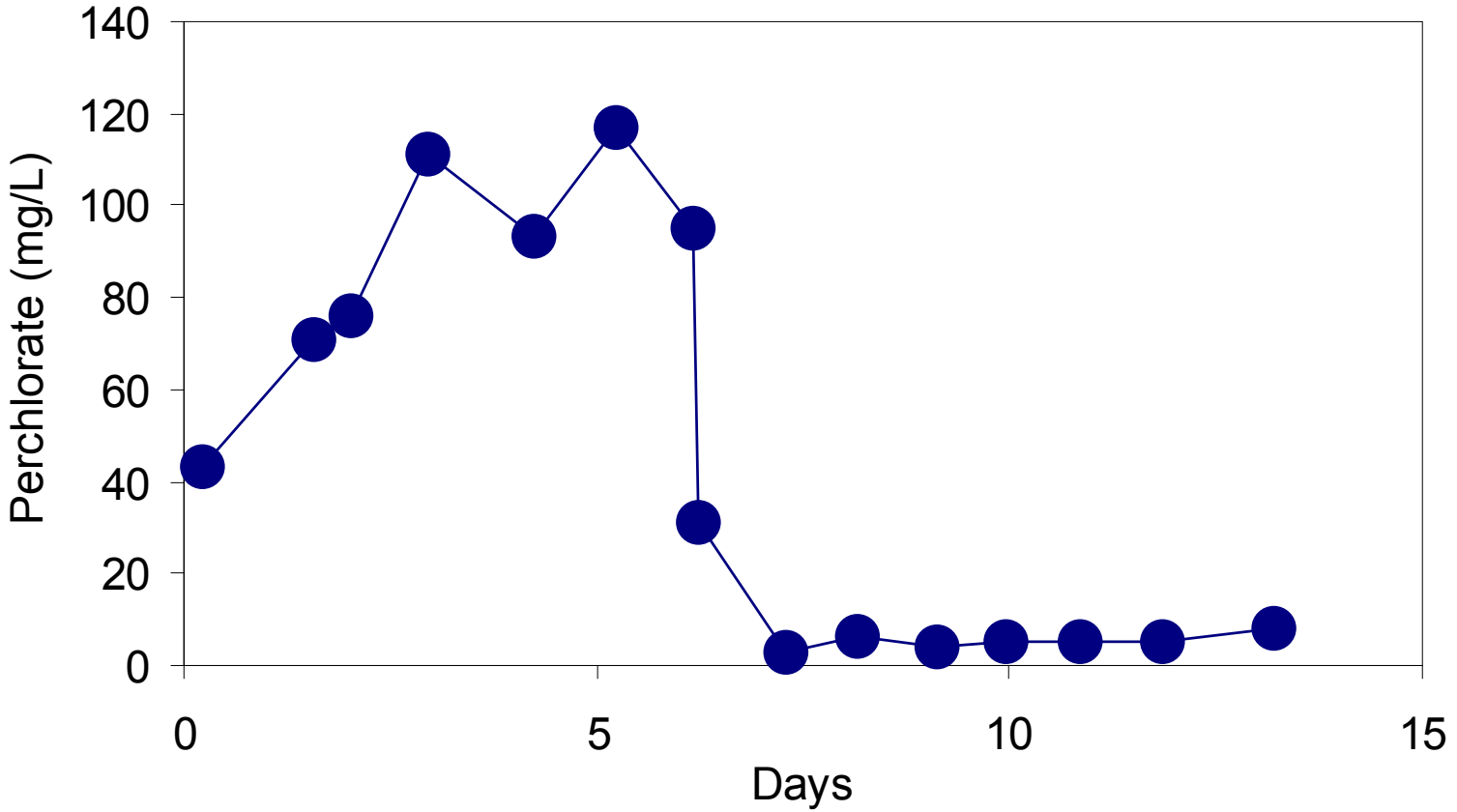
Enrichment in a Chemostat

Wastewater Sample

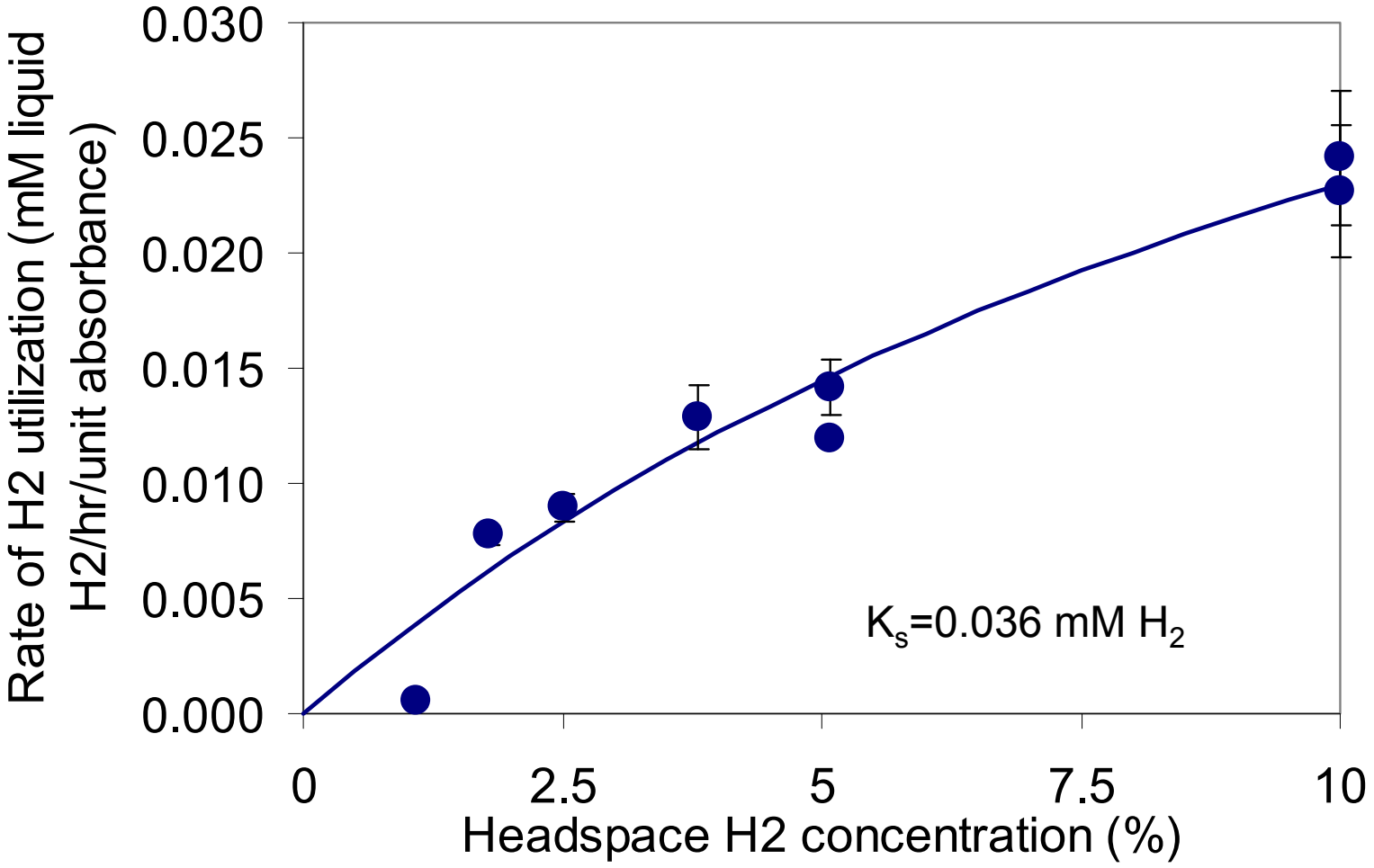


Reactor run in batch mode, and then switched to chemostat mode

Initial reactor performance in chemostat mode (high influent perchlorate concentration)

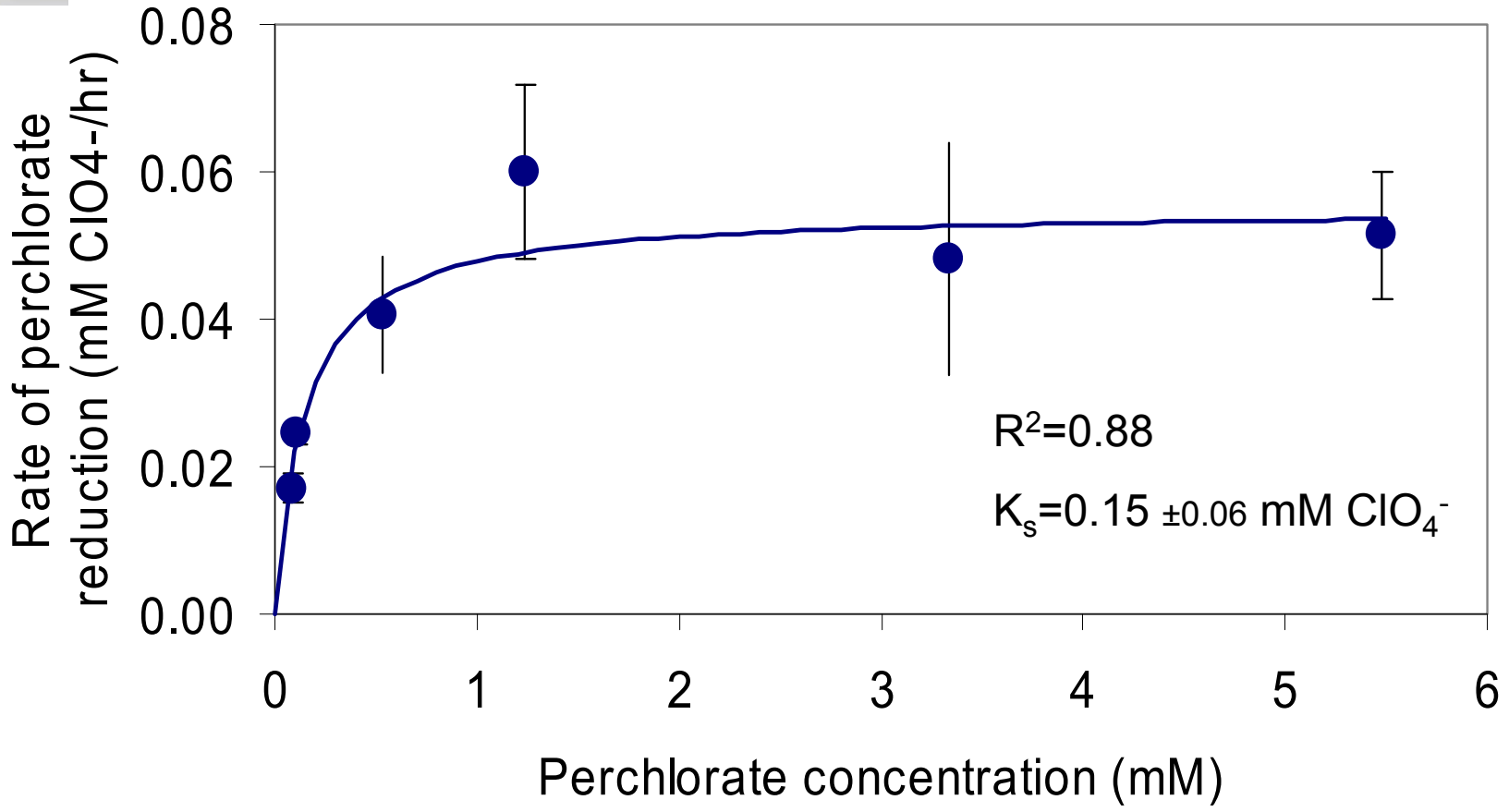


Perchlorate reduction supported by Hydrogen gas: Hydrogen (isolate JM)



From: Miller and Logan (2000)

Perchlorate reduction supported by Hydrogen gas: Perchlorate (isolate JM)



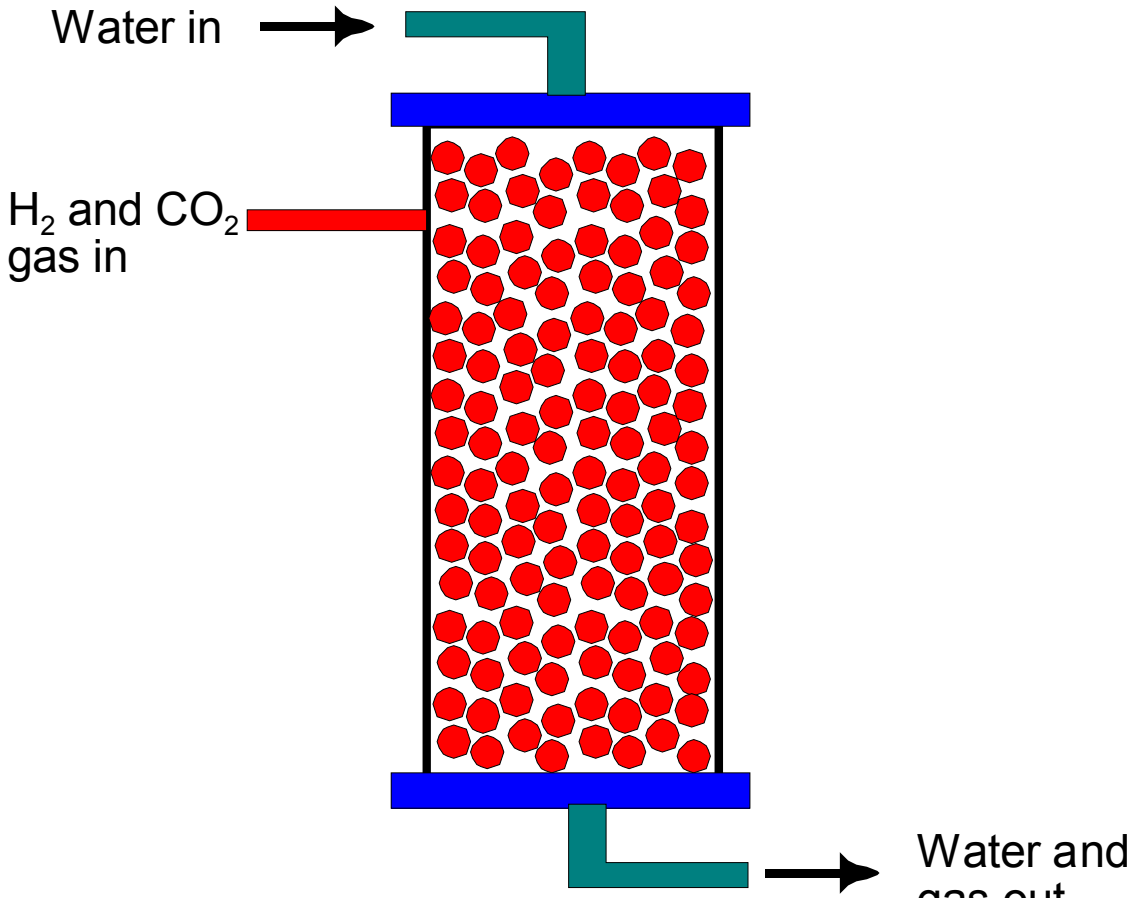
From: Miller and Logan (2000)

Hydrogen Reactor- 1: Proof of Concept

- **Column:** 12.5 cm (10 cm packed), 2.5 cm diameter
- **Packing:** 3 mm diameter glass beads (1200 m^2/ m^3)
- **Pumping Solution:** 740 μg/L perchlorate in trace metal solution
- **Gas mixture:** H_2, 43 mL/min and CO_2, 7.5 mL/min)
- **Operation period**: 145 days

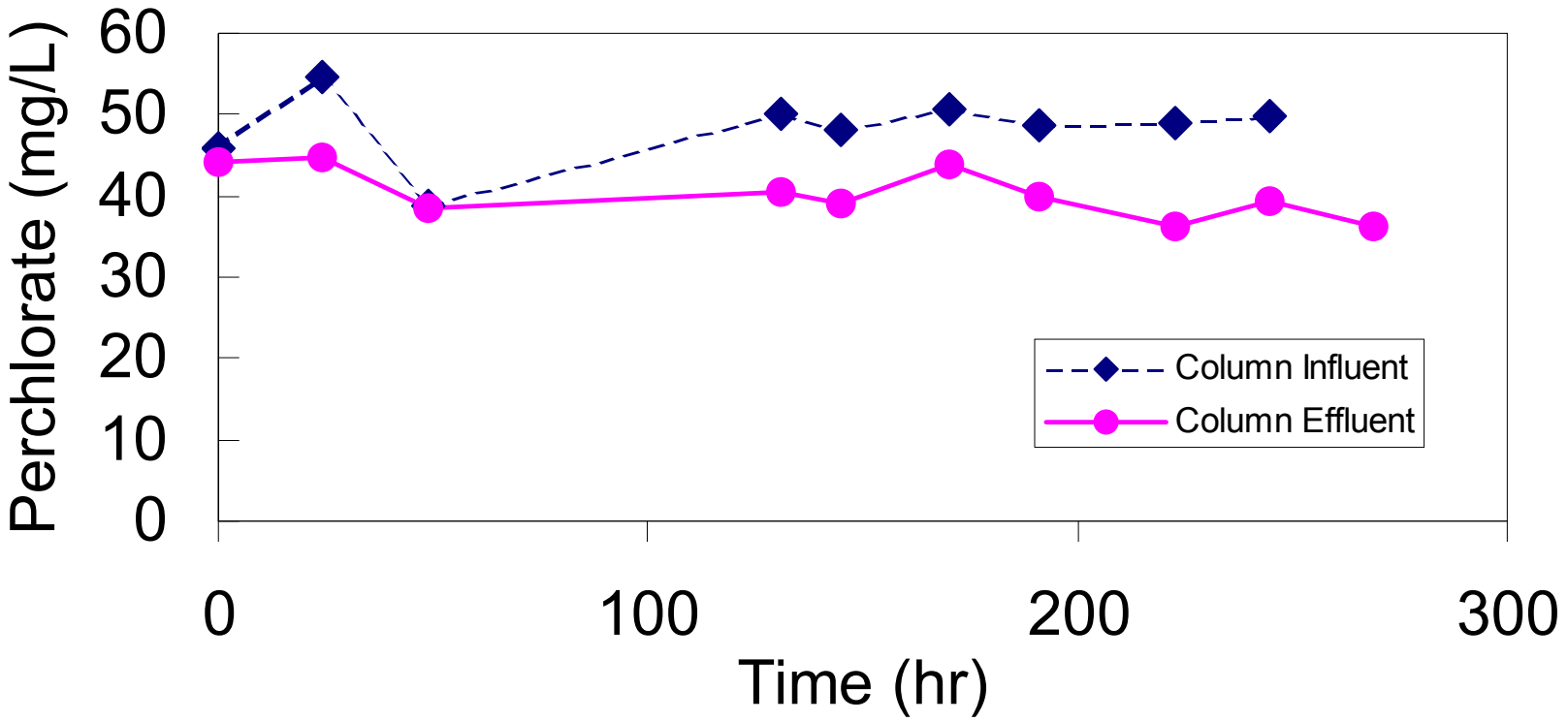
Fixed film biohydrogen reactor

(unsaturated flow)



Initial fixed film reactor performance

High perchlorate concentration (50 mg/L) to build up a biofilm



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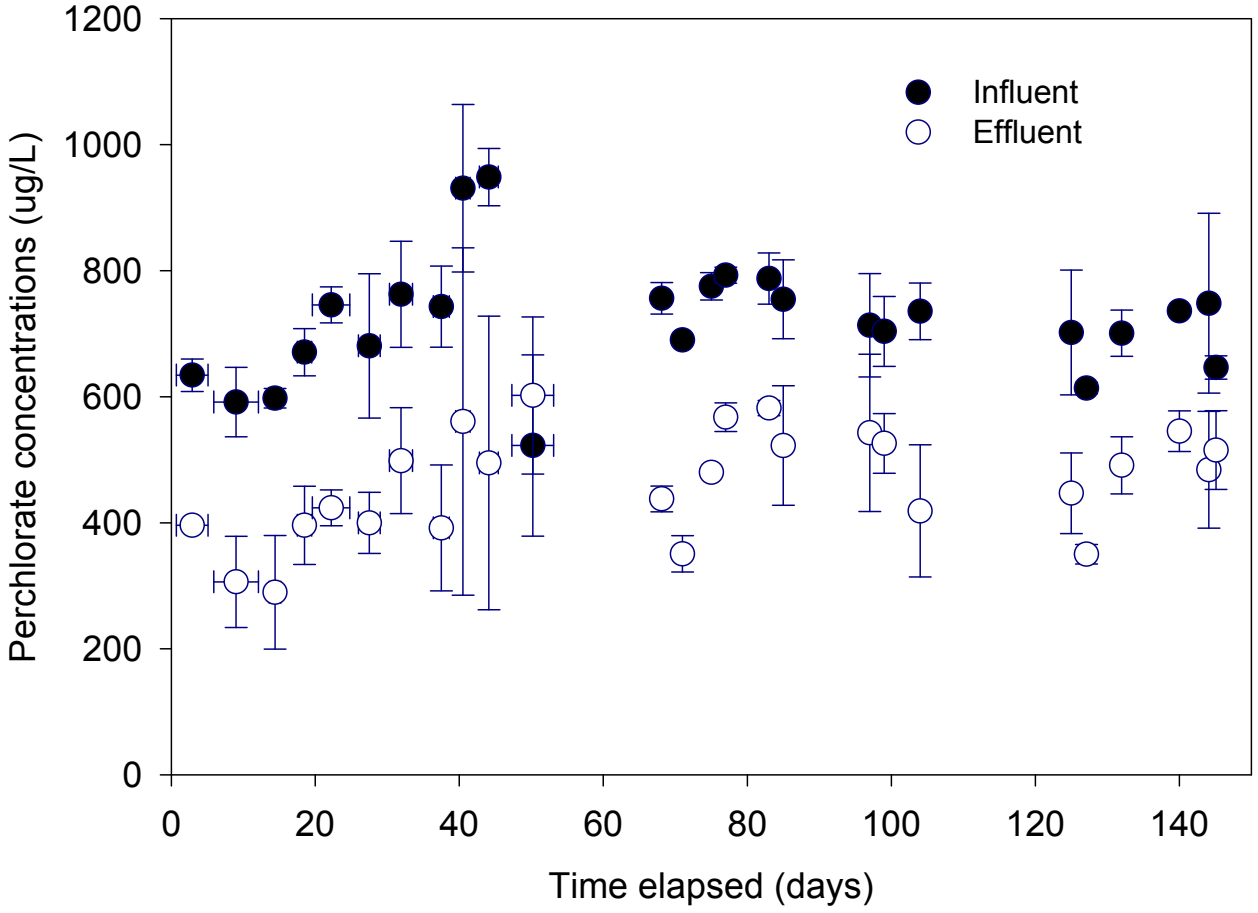
Hydrogen reactor performance

In: 740 ±110 μg/L

Out: 460 ±80 μg/L

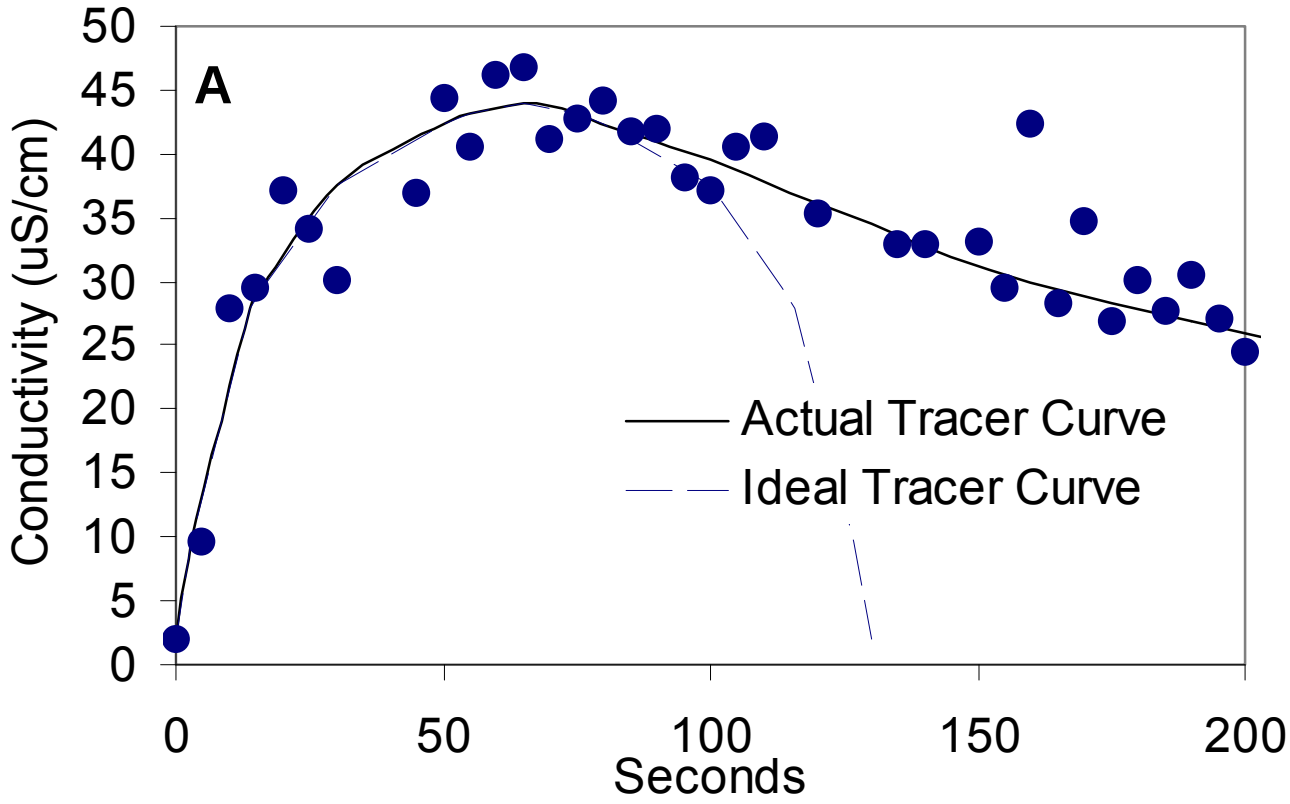
Removal: **38%** ±9%



From: Miller and Logan (2000)

Hydrogen Reactor

Average detention time of 1.0-1.3 minutes



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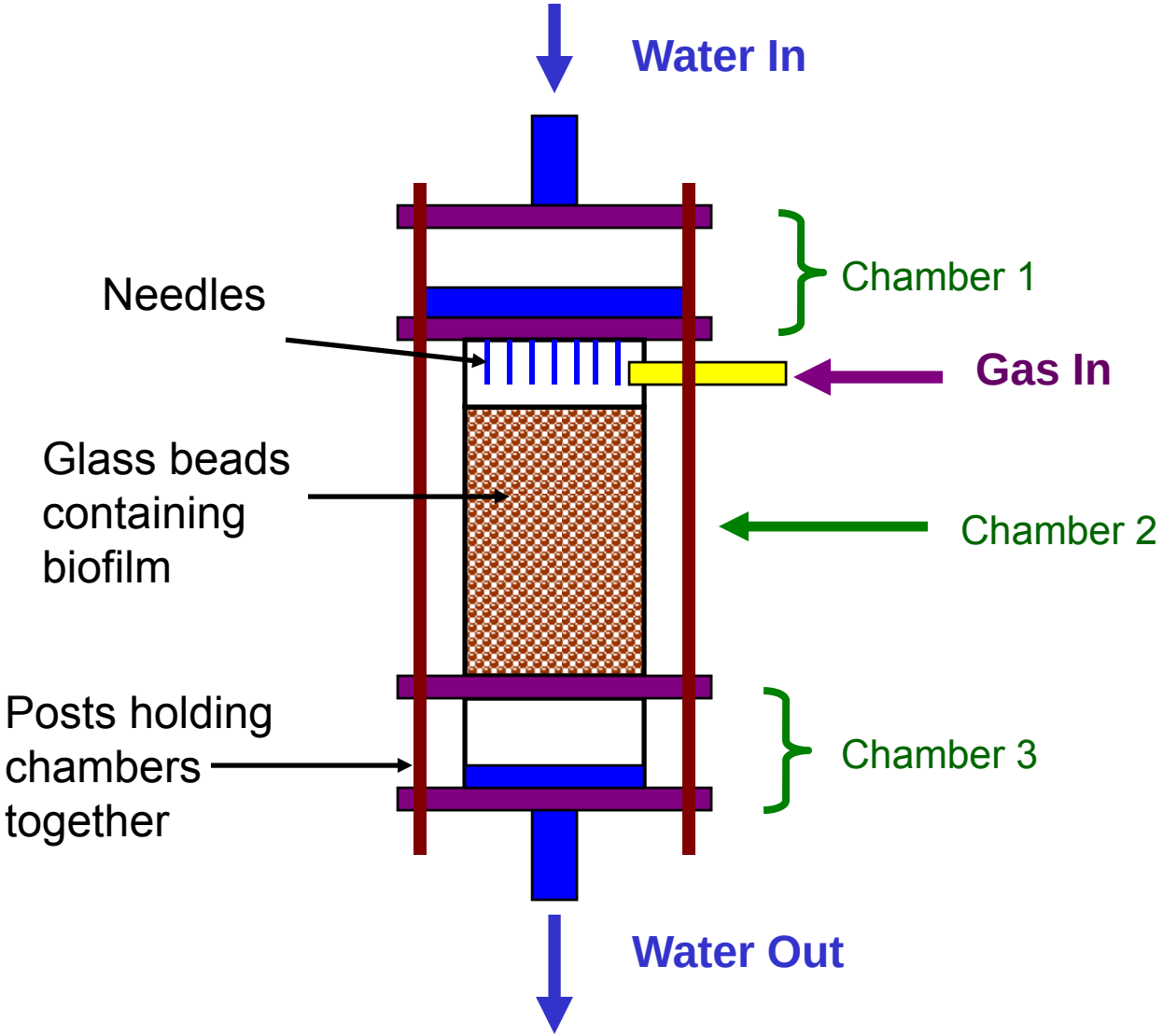
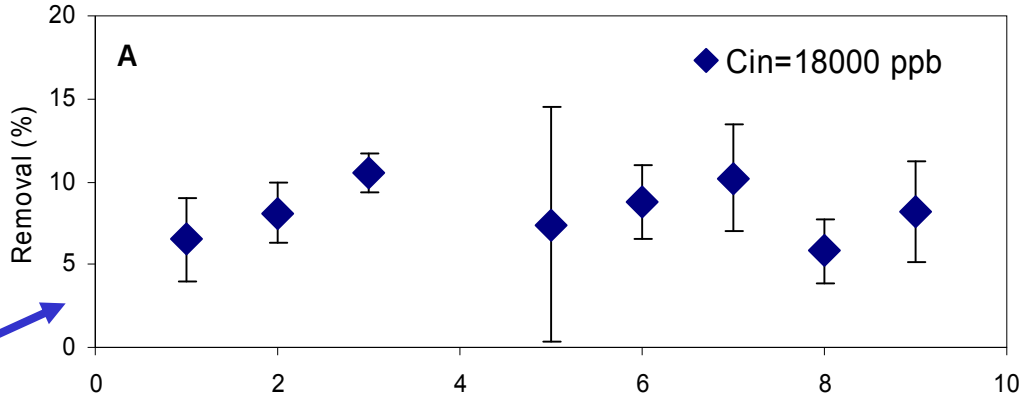
Hydrogen Reactor 2- Three chamber design

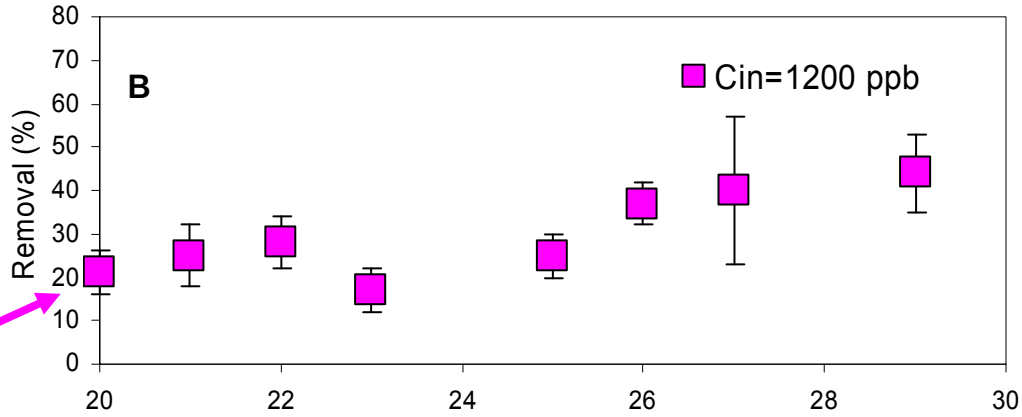


From: Logan & LaPoint (2002)

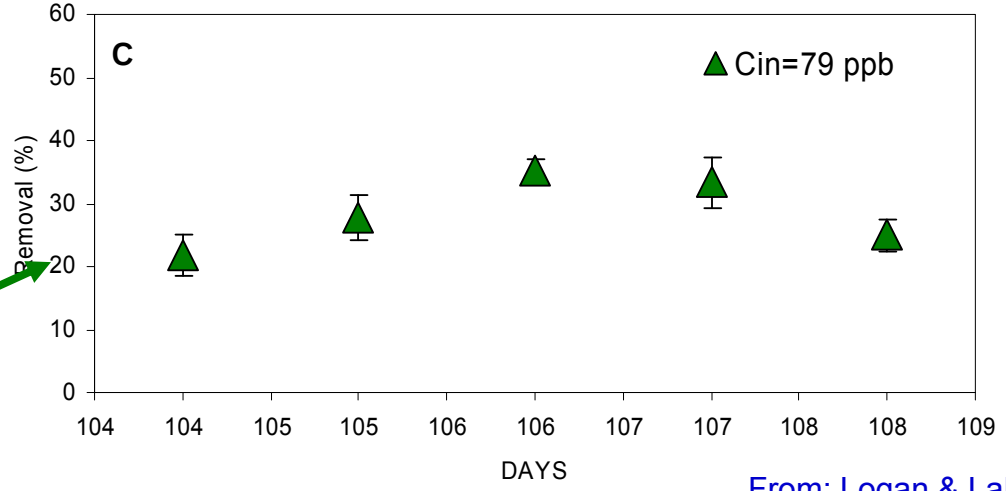
Effect of Influent Perchlorate Concentration on Removal



Removal= 8.2 ±2.9%



Removal= 30 ±7%

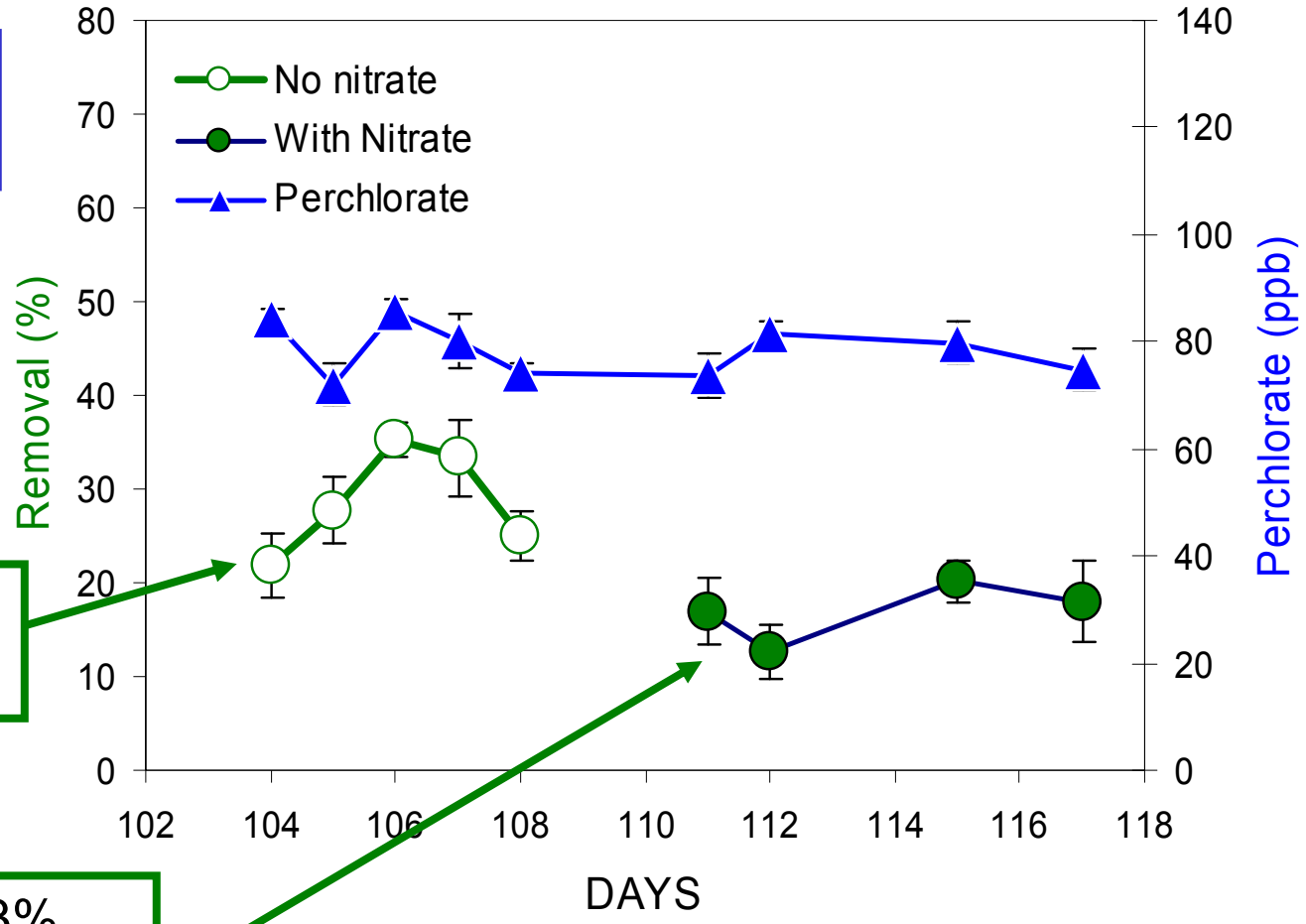


Removal= 29 ±3%

From: Logan & LaPoint (2002)

Effect of Nitrate on Perchlorate Removal

Perchlorate conc.
Influent= 79 ppb



Removal= 29 ±3% no nitrate

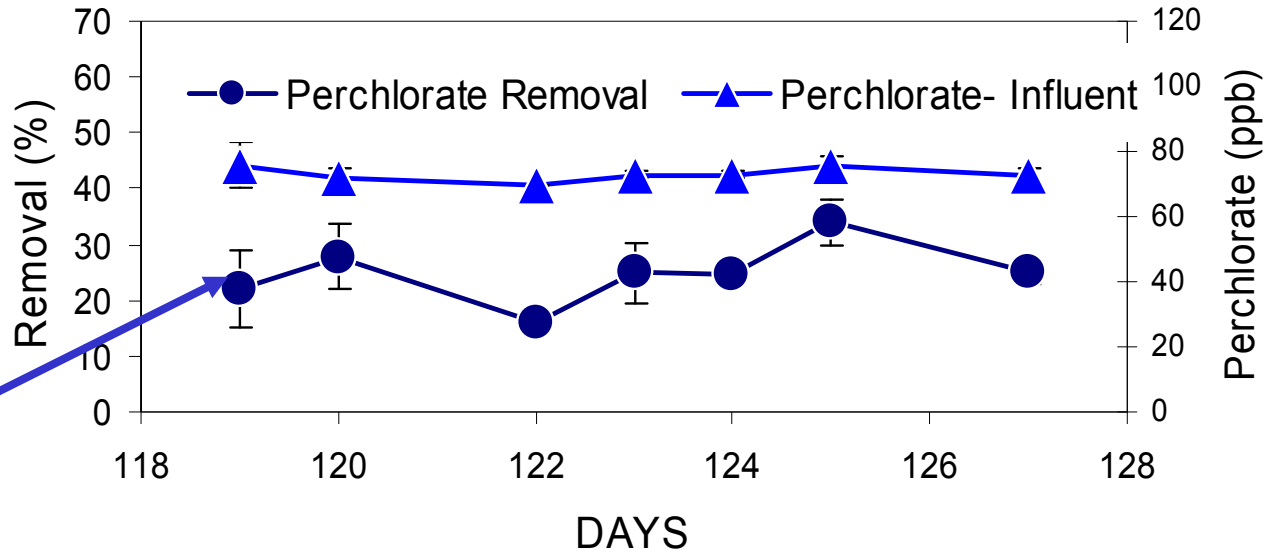
Removal= 17 ±3% with 22 ppm nitrate

From: Logan & LaPoint (2002)

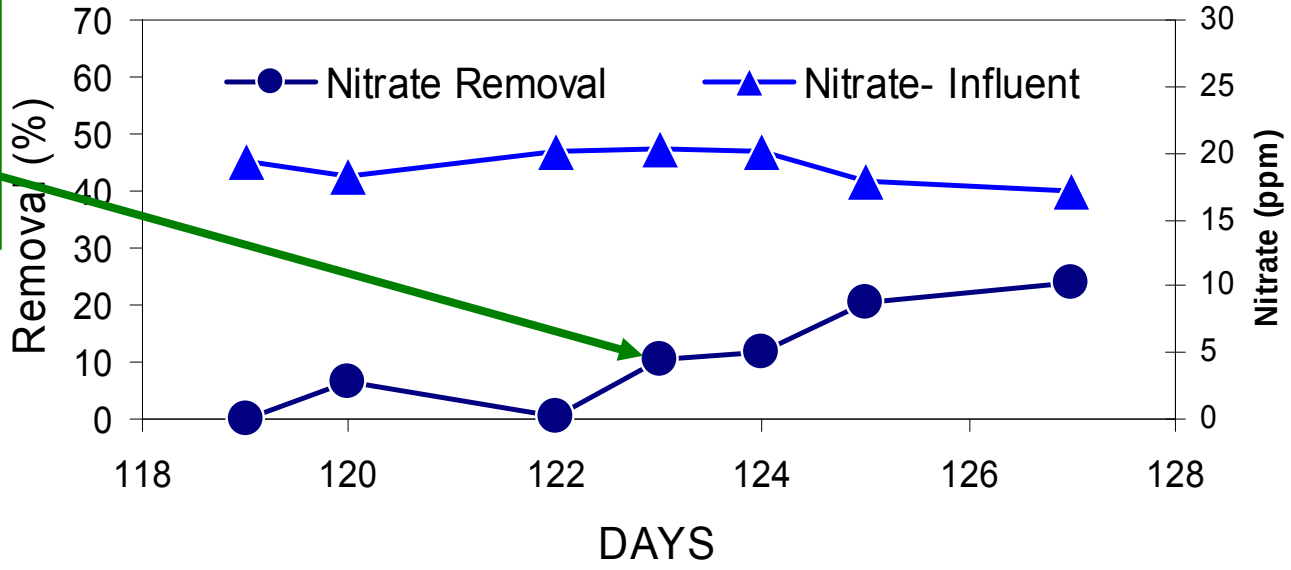
Actual Groundwater from Redlands, CA

Perchlorate (73 ug/L) and Nitrate (21 mg/L) Removal

Perchlorate removal was constant (25 ±5%)



Nitrate removal averaged 10% but may have been increasing



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Reactor Kinetics: Removal Rates

- Expect removal rate, R, is 1st-order with respect to perchlorate concentration.
- Rate calculated as:

$$R = \frac{(Cin - Cout)}{\theta}$$

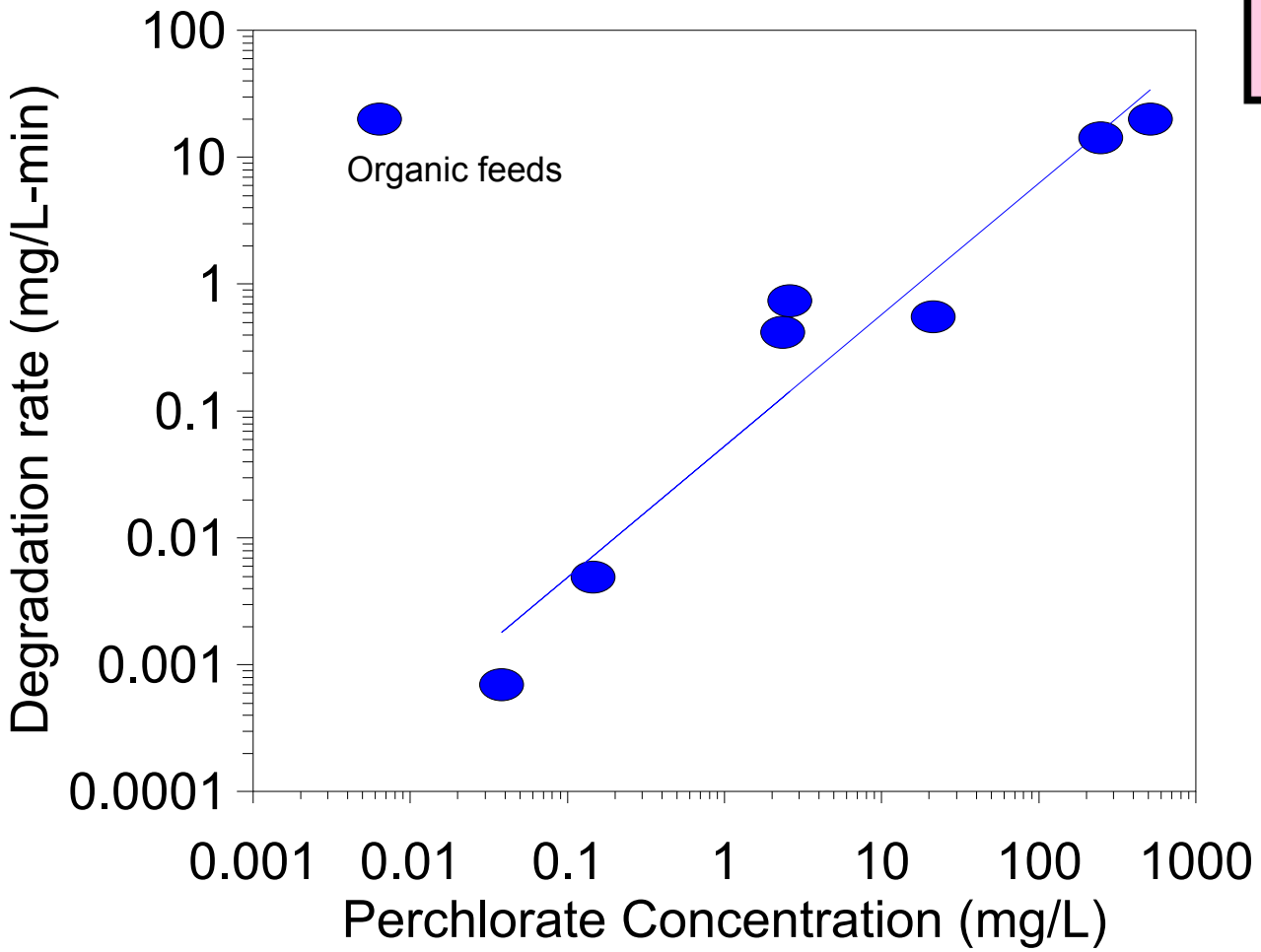
- For 1st-order kinetics, use log mean perchlorate concentration

$$C_{lm} = \frac{C_{in} - C_{out}}{\ln (C_{in} / C_{out})}$$

Perchlorate Removal Rates

(Data prior to 2001; Mixed cultures, organic substrates)

Rate indicates first order kinetics with concentration

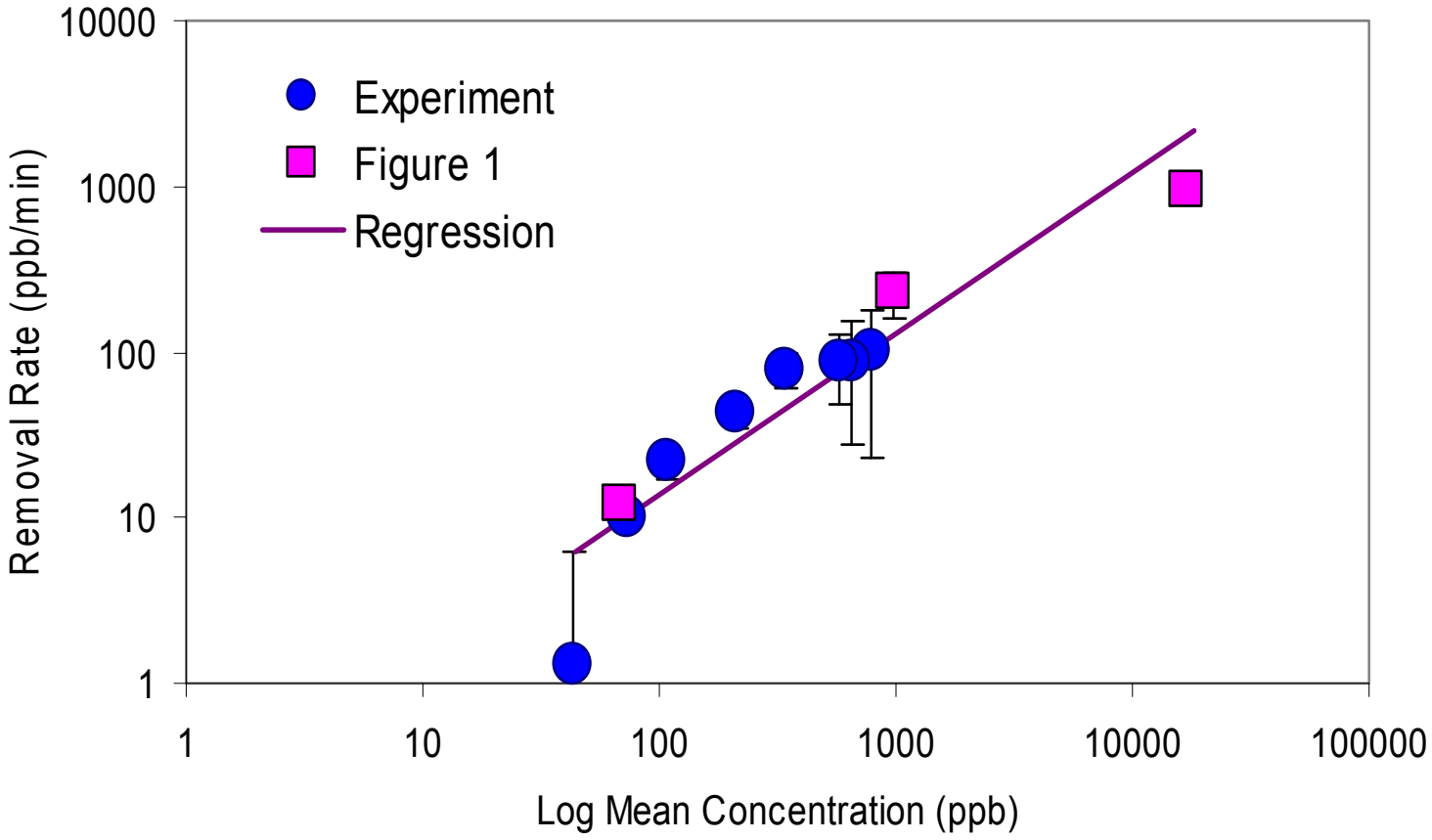


From: Logan (2001)

Perchlorate Removal Rates: H_2 Reactor

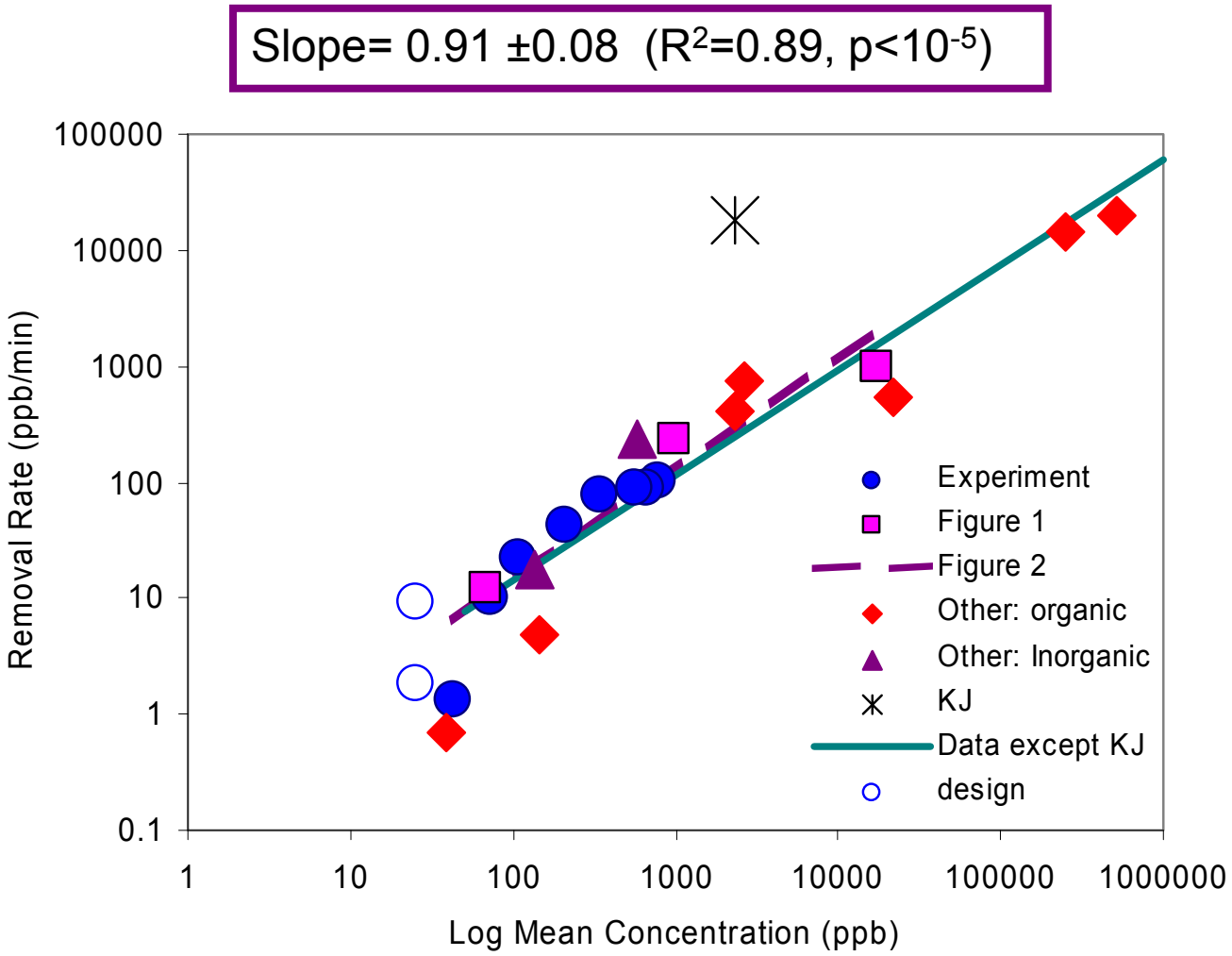
Removal is first-order w.r.t. Perchlorate Concentration

Slope= 0.97 ±0.12 (R^2=0.87, $p<10^{-3}$)



From: Logan & LaPoint (2002)

Removal in Different Bench Scale Fixed Bed Perchlorate Bioreactors



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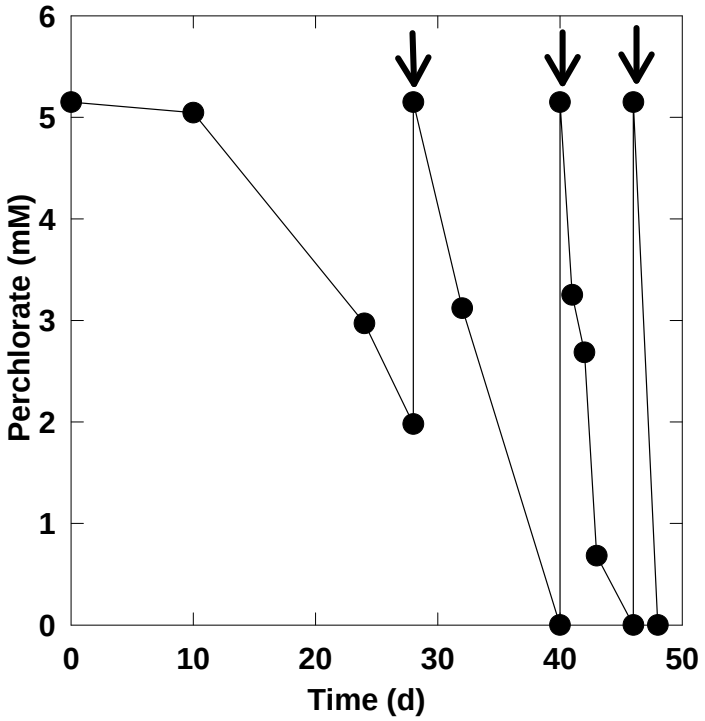
Initial attempt to isolate an autotrophic, perchlorate-respiring bacterium (Joel Miller)

Isolate obtained (*Dechloromonas* sp. JM) that could reduce perchlorate, but did not fix CO_2

Second attempt to isolate an autotrophic, perchlorate-respiring bacterium (Husen Zhang)



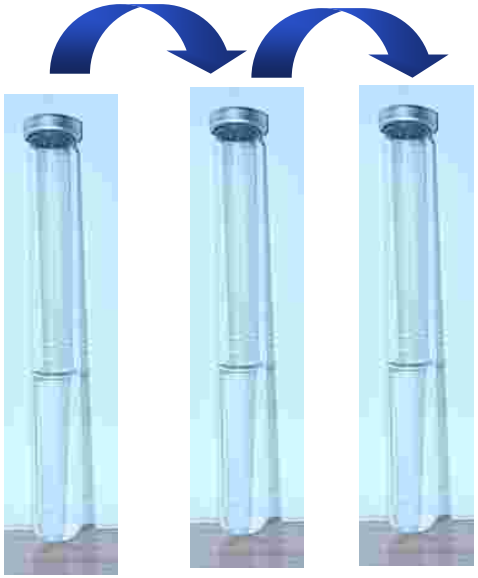
From: Zhang et al. (*In press*)

Second attempt to isolate an autotrophic, perchlorate-respiring bacterium (Husen Zhang)

No isolates fixed CO_2

Second attempt to isolate an autotrophic, perchlorate-respiring bacterium (Husen Zhang)

Dilution to extinction

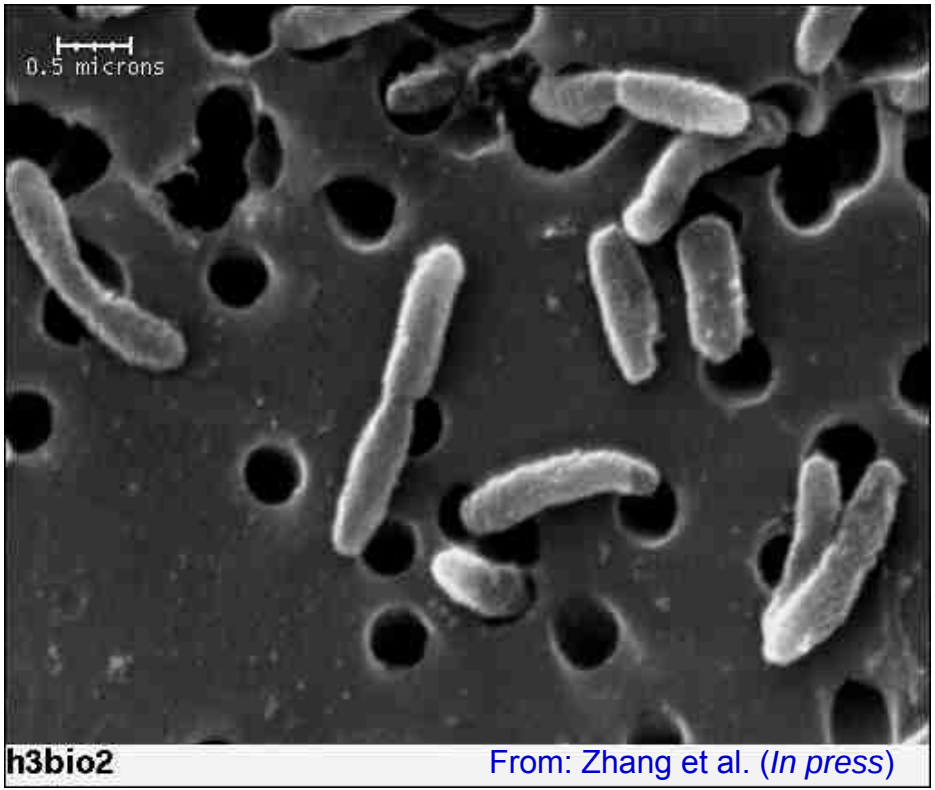


Success!

Isolate could fix CO_2

Isolate obtained: *Dechloromonas sp.* HZ

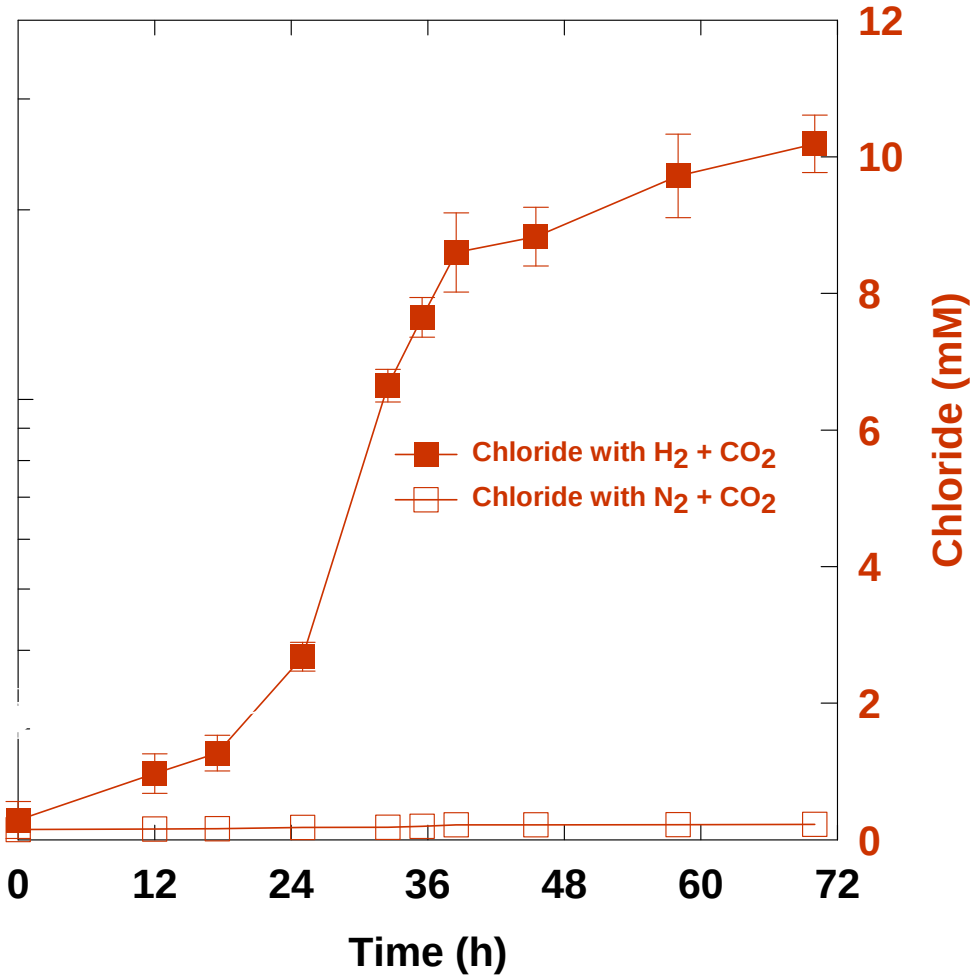
- Uniform morphology: rod, 0.3 × 1.8 μm
- Sequencing indicates pure culture
  - Multiple clones characterized using intergenic transcribed sequence (ITS) show identical sequences.
- No growth in absence of hydrogen or perchlorate



From: Zhang et al. (*In press*)

Autotrophic growth of isolate HZ with perchlorate, H_2, and CO_2

Growth on perchlorate (ClO_4^-) shows complete conversion to chloride

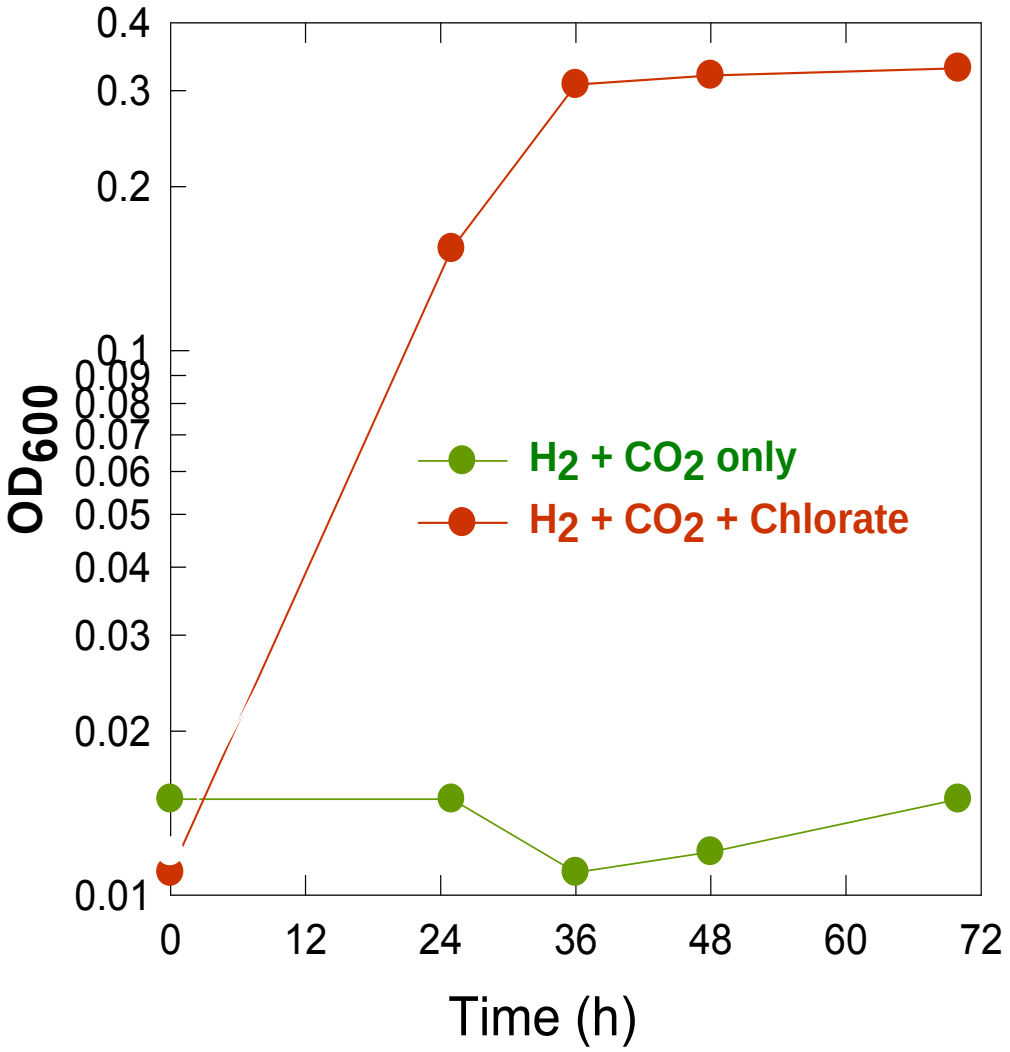


From: Zhang et al. (*In press*)

Growth using alternate e- acceptors

Isolate HZ can use as electron acceptors:

- Oxygen
- Perchlorate
- Chlorate
- Nitrate



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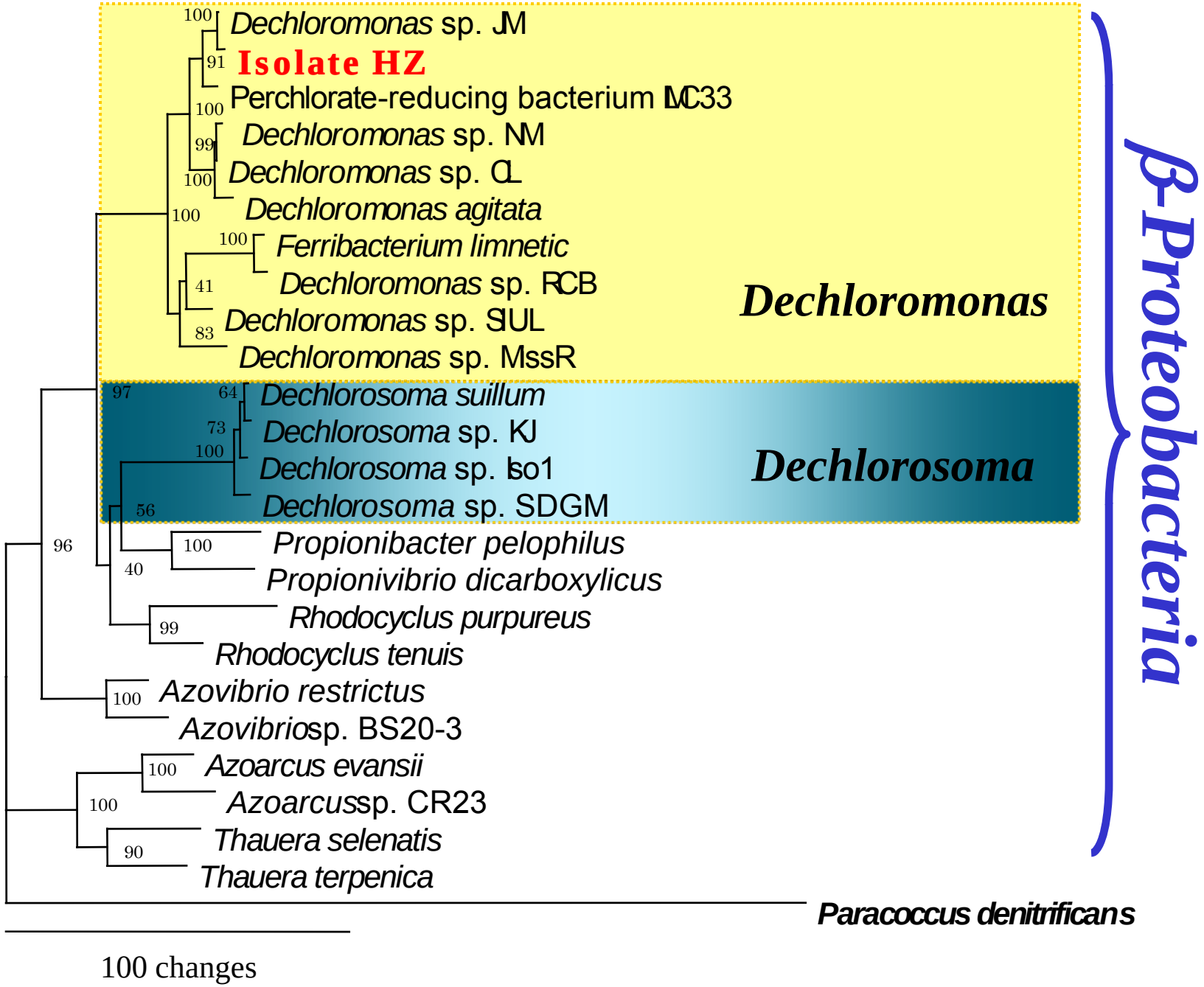

From: Zhang et al. (*In press*)

Scale up of the H_2 Reactor: Pilot Test?

- Laboratory system limited to detention times of only minutes (1.0 – 1.3 min)
- Complete removal of perchlorate at 80 ppb would require detention times of:
  - 18.5 min (first-order, C_{lm}=25.5 ppb)
  - 42 min (95% confidence interval; conservative)
- This would require reactor heights of:
  - 1.5 m (first-order rate)
  - 3.4 m (conservative estimate)
- System would consist of a tank filled with random plastic medium, maintained with a CO_2:H_2 atmosphere.
- No membranes needed
- Collaborator (and funding) is needed for pilot tests.

CONCLUSIONS

- Developed a H_2-gas-phase anaerobic bioreactor that can remove perchlorate from drinking water
- Perchlorate is reduced even in the presence of nitrate at concentrations 3 orders-of-magnitude greater than that of perchlorate.
- Autotrophic perchlorate reduction is possible by isolate *Dechlorosoma* sp. HZ.
- Pilot-scale tests needed to prove the technology in the field.

ACKNOWLEDGMENTS

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REFERENCES

Logan, B.E. and D. LaPoint. 2002. *Wat. Res.* 36(14):3647-3653.

Logan, B.E. 2001. *J. Environ. Engng.* 127(5):469-471.

Miller, J.P. and B.E. Logan. 2000. *Environ. Sci. Technol.* 34(14):3018-3022.

Zhang H., M.A. Bruns, and B.E. Logan. 2002. Perchlorate reduction by a novel chemolithoautotrophic hydrogen-oxidizing bacterium. *Environ. Microbiol., In press.*