Perchlorate Degradation in Bench- and Pilot-Scale Ex-situ Reactors

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Perchlorate Degradation: Topics

- Abundance of perchlorate degrading bacteria.
- Bacterial isolate used in tests: KJ
- Bench-scale reactors: Acetate $\text{H}_2$
- Comparison of rates in bioreactors
- Pilot-scale reactor test
Are perchlorate-respiring bacteria abundant in nature?

One milliliter (1 mL) of water (about one teaspoon) contains:

\[ >10^6 \text{ bacteria} \]

\[ < 1 \text{ perchlorate-reducing microbe (PRM)} \]
Wastewater

Total cells = 8.9x10^7 per ml

From: Wu et al. (2001)
Creek water

**Total cells:** $4.9 \times 10^5$ per ml

**Perchlorate concentration (mg/L)**

- Citric acid
- Molasses
- Lactate
- Acetate

**DAYS**

From: Wu et al. (2001)
Unexposed Soils

2 gram samples

The citrate sample was positive on the 3 other substrates as well

From: Wu et al. (2001)
Unexposed Soils

100 gram samples

Many soils showed perchlorate degradation when a larger sample mass was used.

From: Wu et al. (20...
Perchlorate-contaminated soil

Previous exposure of a soil to perchlorate results in rapid Perchlorate degradation

From: Wu et al. (2001)
PRM Abundance: observations

- PRMs present in natural waters at \(~1000/10^9\)
- PRMs in “pristine” soils, that have no evidence of perchlorate contamination: \(~1/10^9\)
- At sites where perchlorate is present, have an abundant perchlorate reducing population, \(~100/10^9\)
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Phylogenetic analysis of KJ
(courtesy of Dr. Ian Head, Univ. of New Castle)

Classification:
Dechlorosoma sp. KJ

From: Logan et al. (2001)
Permanganate reduces chlorate:

ClO₄⁻ → ClO₃⁻ → ClO₂⁻ → Cl⁻ + O₂

Chlorite and chlorate do not accumulate in water: kD >> kC > kP

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KJ Perchlorate kinetics: $K_s = 33$ mg/L
(lactate grown cell suspensions)

From: Logan et al. (2001)
Substrate kinetics: acetate

From: Logan et al. (2001)
Substrate kinetics: acetate

From: Logan et al. (2001)
Substrate kinetics: acetate

From: Logan et al. (2001)
# Kinetic constants for growth of KJ on acetate

<table>
<thead>
<tr>
<th>Electron Acceptor</th>
<th>$\mu_m$ (h$^{-1}$)</th>
<th>$K_S$ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>0.27 ± 0.02</td>
<td>14 ± 1</td>
</tr>
<tr>
<td>Chlorate</td>
<td>0.27 ± 0.03</td>
<td>60 ± 25</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>0.14 ± 0.01</td>
<td>470 ± 290</td>
</tr>
</tbody>
</table>

From: Logan et al. (2001)
Cell yield - KJ

From: Logan et al. (2001)
Overall Stoichiometry

Without biosynthesis: acetate/perchlorate = 1:1 (mol/mol)
\[ \text{CH}_3\text{COO}^- + \text{ClO}_4^- \rightarrow 2\text{HCO}_3^- + \text{H}^+ + \text{Cl}^- \]

With biosynthesis: acetate/perchlorate = 2.9:1 (mol/mol)
\[ \text{CH}_3\text{COO}^- + 0.35\text{ClO}_4^- + 0.26\text{NH}_4^+ + 0.04\text{H}^+ \rightarrow \]
\[ 0.26\text{C}_5\text{H}_7\text{O}_2\text{N (cells)} + 0.7\text{HCO}_3^- + 0.35\text{Cl}^- + 0.78\text{H}_2\text{O} \]

Epifluorescent micrograph (1000 ×) of KJ stained with acridine orange
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Acetate-Fed Sand Packed-bed Column Experiments

Sampling from the side ports of the column

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Acetate-fed Bioreactors

- **Columns**: 14 cm or 28 cm long.

- **Mixed cultures**: enriched on perchlorate (activated sludge samples)

- **Pure culture**: *Dechlorosoma* sp. KJ

- **Feed**: Artificial groundwater (AGW) containing 20 mg/L perchlorate and nutrients; water from the City of Redlands
Mixed cultures
(14 cm sand column)

Critical EBCT was 34 minutes.

From: Kim and Logan (2000)
Mixed cultures
(28 cm sand column)

Critical EBCT was ~40 minutes.

From: Kim and Logan (2000)
Pure culture: KJ
(28 cm-sand column)

Critical EBCT was \(~2.1\) minutes.

From: Kim and Logan (2001)
Pure culture: KJ
(28 cm-sand column)

As EBCT decreased:
Perchlorate was non-detectable for 84% of samples (n=147)

From: Kim and Logan (2001)
Pure culture: KJ
(28 cm-sand column)

Reliability: After start up, perchlorate removal was stable at:
- 95% of time: <23 ppb
- 84% of time: <4 ppb

From: Kim and Logan (2001)
Perchlorate is completely removed using groundwater from Redlands site.

B. Logan, Penn State University

From: Kim and Logan (2001)
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Perchlorate reduction supported by Hydrogen gas

Rate of H₂ utilization (mM liquid H₂/hr/unit absorbance) vs. Headspace H₂ concentration (%)

From: Miller and Logan (2000)
Hydrogen Reactor

- **Column**: 12.5 cm (10 mm packed), 2.5 cm diameter
- **Packing**: 3 mm diameter glass beads (1200 m²/ m³)
- **Pumping Solution**: 740 μg/L perchlorate in trace metal solution
- **Gas mixture**: H₂, 43 mL/min and CO₂, 7.5 mL/min
- **Operation period**: 145 days
Fixed film biohydrogen reactor
(unsaturated flow)

Water in

$H_2$ and $CO_2$

gas in

Water and
gas out
Hydrogen Reactor

Average detention times of 1.0-1.3 minutes

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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)
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Reactor Kinetics: Removal Rates

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

$$ R = \frac{(C_{\text{in}} - C_{\text{out}})}{\theta} $$

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

$$ C_{\text{lm}} = \frac{C_{\text{in}} - C_{\text{out}}}{\ln \left( \frac{C_{\text{in}}}{C_{\text{out}}} \right)} $$
**Perchlorate Bioreactor Rates**
(Data prior to 2001; Mixed cultures, organic substrates)

Rate indicates first order kinetics with concentration

From: Logan (2001)
HYDROGEN REACTOR

H$_2$ reactor rates are slightly higher than those in other types of reactors

From: Logan (2001)
ALL PERCHLORATE BIOREACTOR
REMOVAL RATE DATA
(Sand Column Reactor Data)

The pure culture rate is an order-of-magnitude greater than other rates at comparable perchlorate concentrations.

Pure culture (KJ) reactor

Adapted from Logan (2001)
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Study Participants

- **Site**: Redlands, California, Texas St well field
- **Engineering Firm**: Camp, Dresser and Mc Kee
- **Research Unit**: The Pennsylvania State University
- **Funding Agency**: American Water Works Association Research Foundation (AWWARF; via an EPA Grant)
Study site: City of Redlands

Map from the University of Redlands website
Texas St. Site in Redlands has 24 GAC columns (shut down due to perchlorate breakthrough)
PERCHLORATE FIXED-BED BIOREACTOR
Patent No. 6214607

Contaminated water source

Supplemental carbon source with (optional) N, P addition

Perchlorate respiring culture (optional)

Backwash with chlorate, N, P, acetate

Sand filter

ATTRIBUTES:
Continuous perchlorate removal
Clogging avoided by intermittent backwash
Biofilm regeneration by side process

Perchlorate free water
Pilot plant Specifications

• **Feed**: groundwater, acetic acid, ammonium phosphate
• **Two bioreactors in parallel**:  
  – Sand  
  – Plastic media
• **Monitoring**:  
  – flow, pressure, pH, dissolved oxygen,  
  – Perchlorate, acetate, nitrate
Media Used in Two Reactors operated in parallel

Tri-Pack Plastic Media  Sand (1 mm diameter)

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Raw water supply - Redlands Site
Bioreactors housed on site in a converted garage (Redlands, CA)
Filter inlet controls
In line mixers, flow measurement, and flow controller
Filter pumps, one for each reactor
Water exits at reactor top (via an overflow weir) to a drain
Water then goes to a holding tank that is periodically emptied.
Water quality monitoring panel
Monitoring water quality

Dissolved oxygen, pH, and conductivity at any location

Influent pH after acetate addition

B. Logan, Penn State University
Samples can be obtained along each reactor
The reactors can be backwashed and air scour used to mix media.

B. Logan, Penn State University
Preliminary Pilot Plant Results

• Two bioreactors are just in startup phase (running about 2 weeks)
• Flow is 1 gpm/reactor
  - Sand column: 20 min detention time
  - Plastic media: 60 min detention time
• During this startup phase, perchlorate was reduced from 70 ppb to:
  - Sand column: 10 ppb initially, <4 ppb after first backwashing
  - Plastic media: 40 ppb initially, <4 ppb after first backwashing
Preliminary Pilot Plant Results

- **Dissolved oxygen:** completely removed
- **Effluent pH:** 6.7 – 6.9
- **Turbidity:** 2-4 NTU
- **Nitrate:** evidence of gas bubbles
- **Odors:** none during operation
CONCLUSIONS

• Perchlorate reducing microbes are present in natural water and soil samples, but enriched in perchlorate-contaminated soils.

• It is possible to obtain high perchlorate removal rates, at low EBCT of 2.1 min, in packed bed reactors inoculated with pure culture (KJ)
CONCLUSIONS... continued

• Perchlorate removal was achieved in the laboratory using groundwater from the Redlands site, containing dissolved oxygen and nitrate.

• Pilot scale tests are underway in Redlands California to demonstrate the reliability of perchlorate removal using a large scale reactor and actual groundwater sample.
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References


