In Situ Electrochemical Generation of Ferrate for Water Treatment

Presentation to

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Motivation

- Reactive innovations is a small business focused on developing electrochemical technologies such as : electrolysis, fuel cells, reactive separations, advanced water treatment
- Environmental regulation are prompting new innovations in water treatment
- In the future, both centralized and decentralized water treatment must avoid the use of chlorine
- This work came about because of the Navy's need for onboard waste water processing treatment which resulted in a research and development program
  - The next generation of Navy combatants will utilize modular mission packages to provide focused mission capability and facilitate technology refresh.
  - The littoral combat ship (LCS) is the first of the US Navy's next generation surface combatants. Intended as a relatively small surface vessel for operation in the littoral region (close to shore), the LCS is smaller than the Navy's guided missile frigates and have been compared to the corvette of international usage.

Wastewater Processing options

- Current commercial technologies include biological, physical/chemical and advanced oxidation treatments
  - Require large tanks
  - Not tested with high levels of contaminants
  - Typically not rapid-start systems.
- Advanced technologies must also be incompliance with EPA to limit discharge of contaminated waste streams into natural waters
  - Process must reduce contaminants to acceptable levels
    - ex. fecal coliform bacteria count to 100 in 100 mls
  - Process must not add unwanted chemicals
    - MEPC 55 discourages the use of chlorine or chlorine-based derivatives.
  - Favored oxidizing agents have included oxygen, ozone, and hydrogen peroxide
- **Our approach is based on a strong oxidizing agent which meets the environmental requirements: ferrate**

Ferrate background

- **What is Ferrate?**
  - Iron in its familiar form exists in the +2 and +3 valence state
  - Higher valence states are generated as oxyanions of iron
  - iron in the +6 state is FeO_4^{-2}, also called ferrate
- **Redox potentials have been determined in both acidic and basic media**
  - $FeO_4^{-2} + 8H^+ + 3e^- \rightarrow Fe^{+3} + 4H_2O$ $E_o = +2.2$ V (1)
  - $FeO_4^{-2} + 4H_20 + 3e^- \rightarrow Fe^{+3} + 8OH^-$ $E_o = +0.72$ V (2)
  - Ferrate species is perhaps the most powerful oxidizing compound that can be used in normal applications with a higher potential in acid media than either ozone (2.04V) or chlorine ~1.4 V)
- **Effectiveness of Ferrates in treating wastewater has been well reported:**
  - Removes toxic organic molecules such as alcohols, nitrosoamines, phenol, nitrilotriacetic acid
  - Removes inorganic ions such as cyanide
  - Destroys viruses
  - Destroys bacteria
- **Ferrate is self- removing and produces a benign product**
  - It will react with water via
    - $4\ FeO_4^{-2} + 10\ H_20 \rightarrow 4Fe^{+3} + 20\ OH^- + 3O_2$
  - In all oxidation reactions, final product is the non-toxic ferric ion which forms hydroxide oligomers which act can act as a flocculating agent
- **Ferrate can be prepared through chemical or electrochemical means through well known procedures**
- **Why is Ferrate not widely used?**
  - High oxidation state leads to highly reactive unstable commodity
  - Ferrate is typically produced in highly alkaline media to suppress decomposition
  - Separation and purification process are required
  - Expensive process to stabilize the end product
  - Commercial attempts to generate reasonably priced ferrate compounds have failed to date

Our Technical Approach

- *In Situ* Electrochemical Generation of Ferrate
  - Generate and use ferrate in a flowing electro-oxidation decontamination reactor
- Eliminates stability issue
  - lifetime of ferrate in aqueous solutions has been measured:
    - half-life in 10 M NaOH is 270 h
    - half-life in 1 M NaOH is 180 s
- Our approach does not regard ferrate as a long-lived bulk chemical but as a *transient* electrochemically mediating species

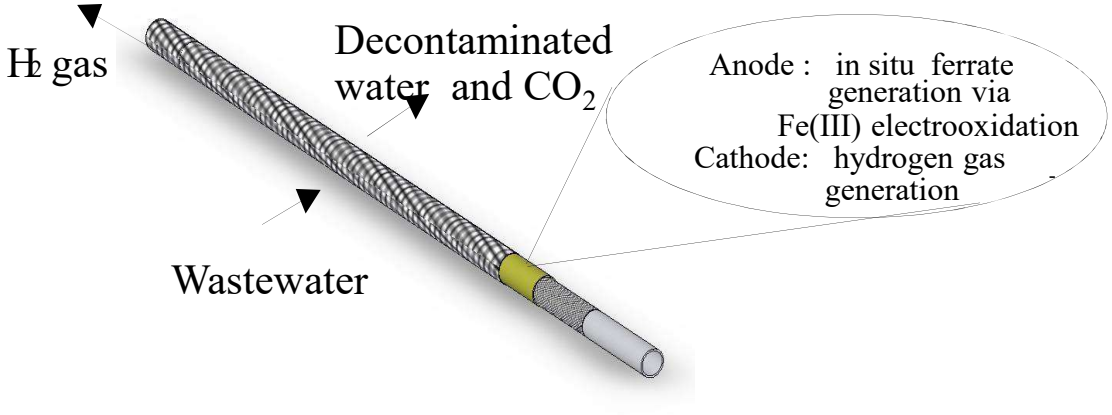
- By producing and consuming ferrate in the same reactor, the required lifetime will not necessitate a high pH

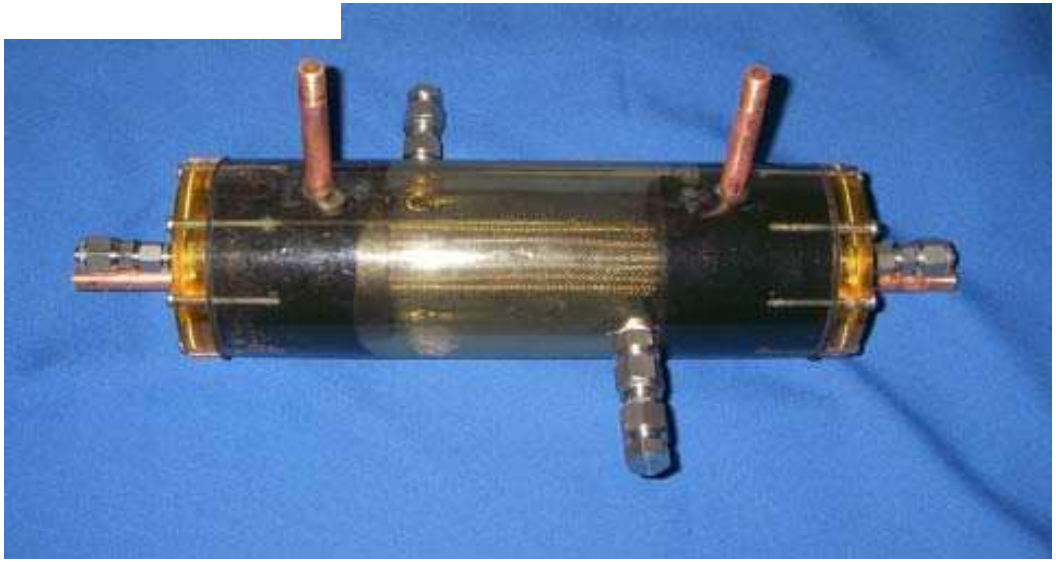
Electrochemical Generation of Ferrate

- Ferrate can be electrochemically generated using iron metal or ferric oxide in both alkaline and acid media:
- Alkaline media
  - ferric oxide starting material:
    - Anode : $0.5(Fe_2O_3\text{-}H_2O) + 5OH^- \rightarrow FeO_4^{-2} + 3H_20 + 3e^-$
    - Cathode: $3H_2O + 3e^- \rightarrow 3OH^- + H_2$
  - Iron metal starting material
    - Anode: $Fe + 8OH^- \rightarrow FeO_4^{-2} + 4H2O + 6e^-$
    - Cathode: $6H_2O + 6e^- \rightarrow 6OH^- + 3H_2$
- Acid/neutral environment:
  - Ferric oxide starting material
    - Anode: $0.5(Fe_2O_3\text{-}H_2O) + 2H_20 \rightarrow FeO_4^{-2} + 5H^+ + 5e^-$
    - Cathode $5H^+ + 5e^- \rightarrow 3H_2$
- In our approach, electrochemically produced ferrate oxidizes contaminants and is reduced to an iron species
  - Eg. Ferrate oxidizes methanol to carbon dioxide and water via
    - $FeO_4^{-2} + CH_3OH \rightarrow Fe(OH)_3 + CO_2 + 2OH^-$

Tubular Decontamination Reactor

based on RIL micro-tubular manufacturing technology





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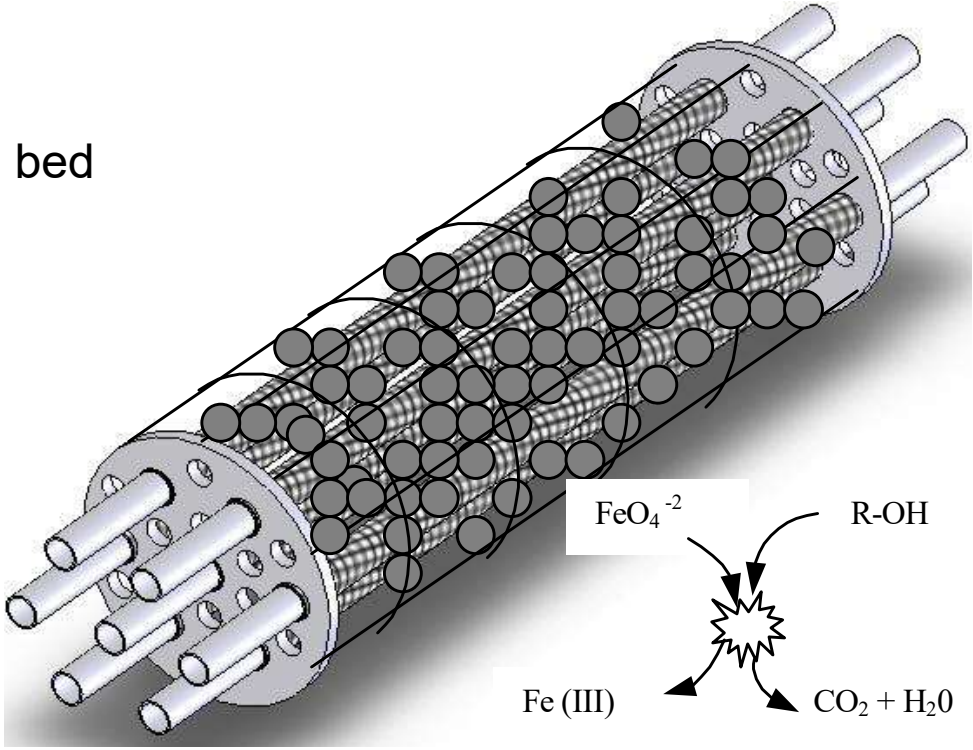
Electrochemical Decontamination Reactor

- Incorporates a packed bed anode
  - Iron or iron oxide
- Wastewater flows through the packed bed
- Voltage is applied
- Ferrate is generated
- Ferrate reacts with contaminants



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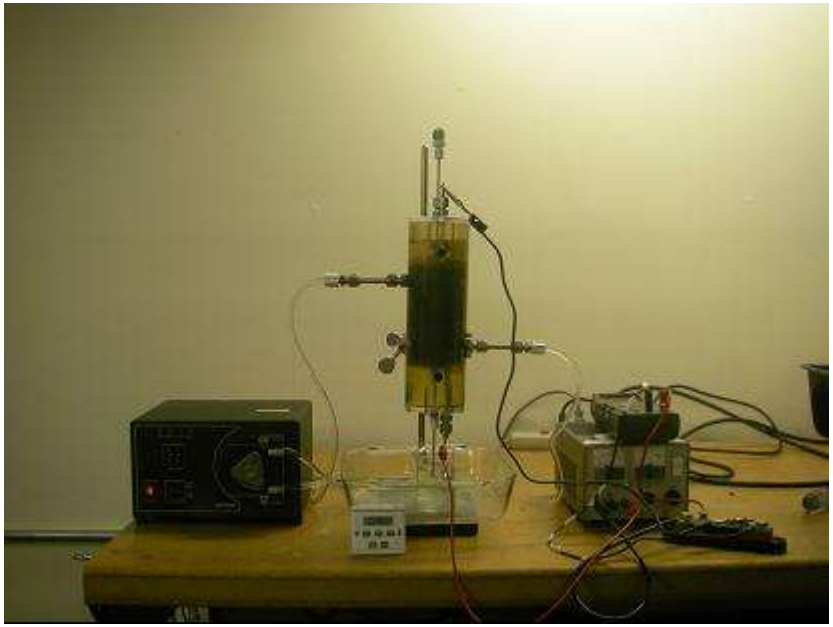
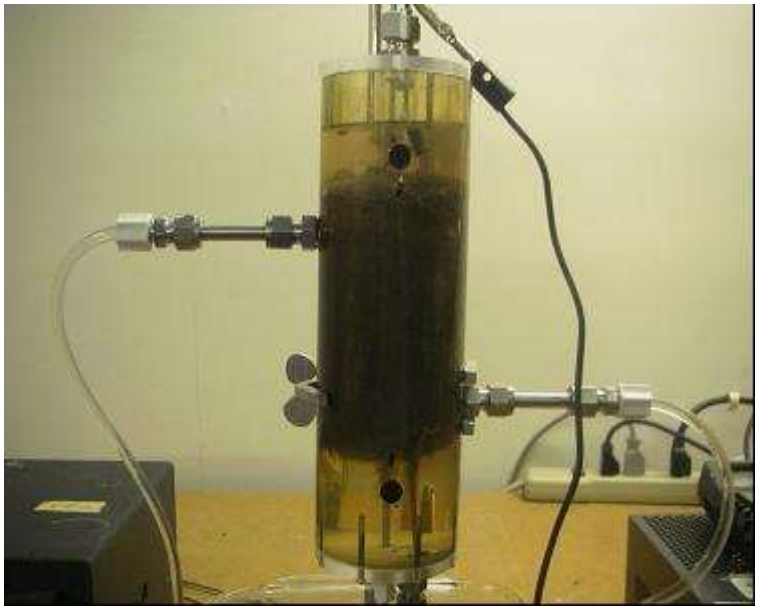
Analysis methods

- Chemical Oxygen Demand: primary indicator of phase I reactor effectiveness
  - Measured in house using EPA-approved colorimetric method
    - BioScience Accutest COD test kit
  - Thorstensen Analytical Laboratory
    - EPA approved Hach 9000
- Biochemical oxygen demand
  - Estimated in house by COD/BOD ratio
  - Thorstensen Analytical laboratory performed final analysis
    - BOD(5) test method SM 5210B
- Fecal Coliform
  - Thorstensen Analytical laboratory performed final analysis

Initial Single Tube MEA Test Reactor





Test progression

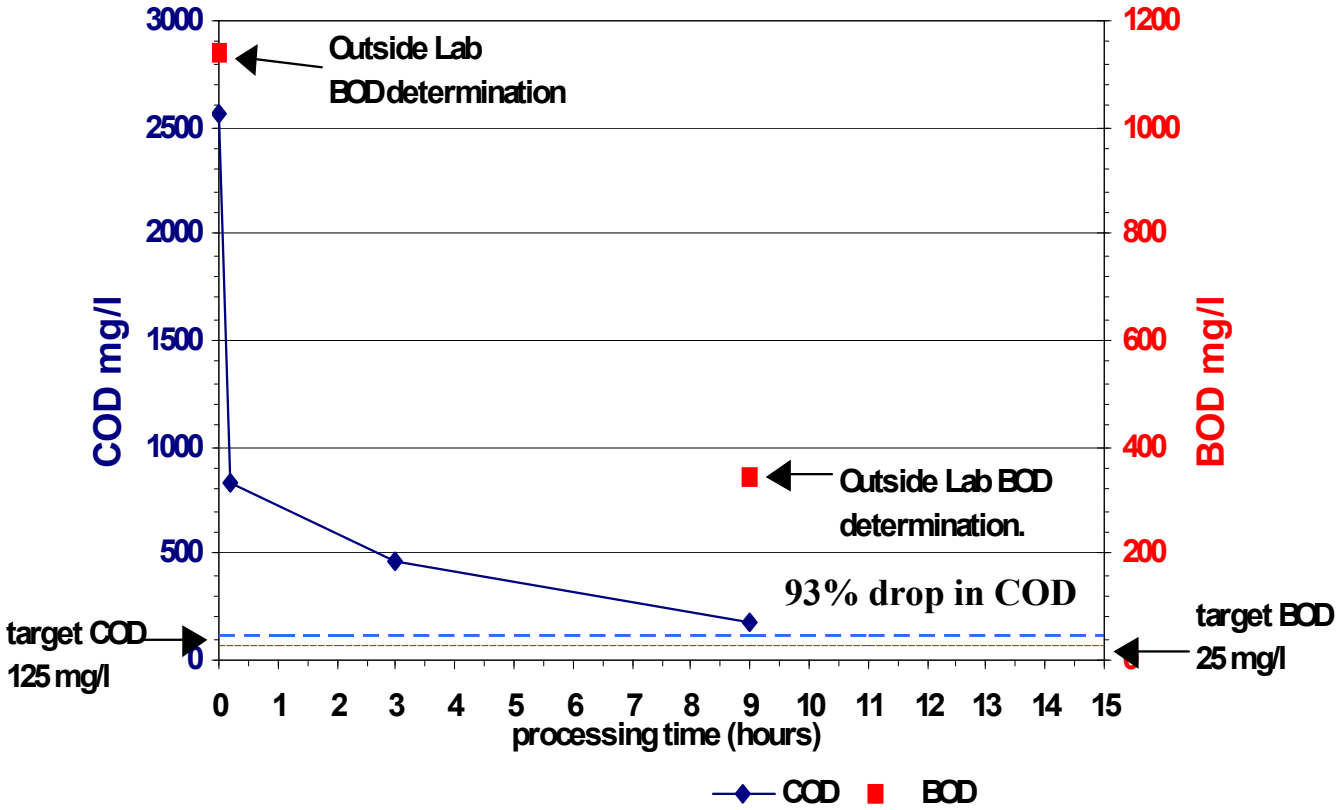
1. Produced ferrate in 4 M NaOH, pH>14
2. Processed simulated laundry wastewater pH = 9
3. Processed graywater using Navy recipe pH= 7

(Diluted graywater simulant to obtain initial COD values in desired range)

4. Processed blackwater from municipal treatment facility

4 Tube Array
Processing graywater

- 4 tubes in parallel
- Cell potential:2.4V
- Current : 7 amps
- Test solution: grey water simulant pH neutral
- Re-circulating flow rate: 225 mls/min



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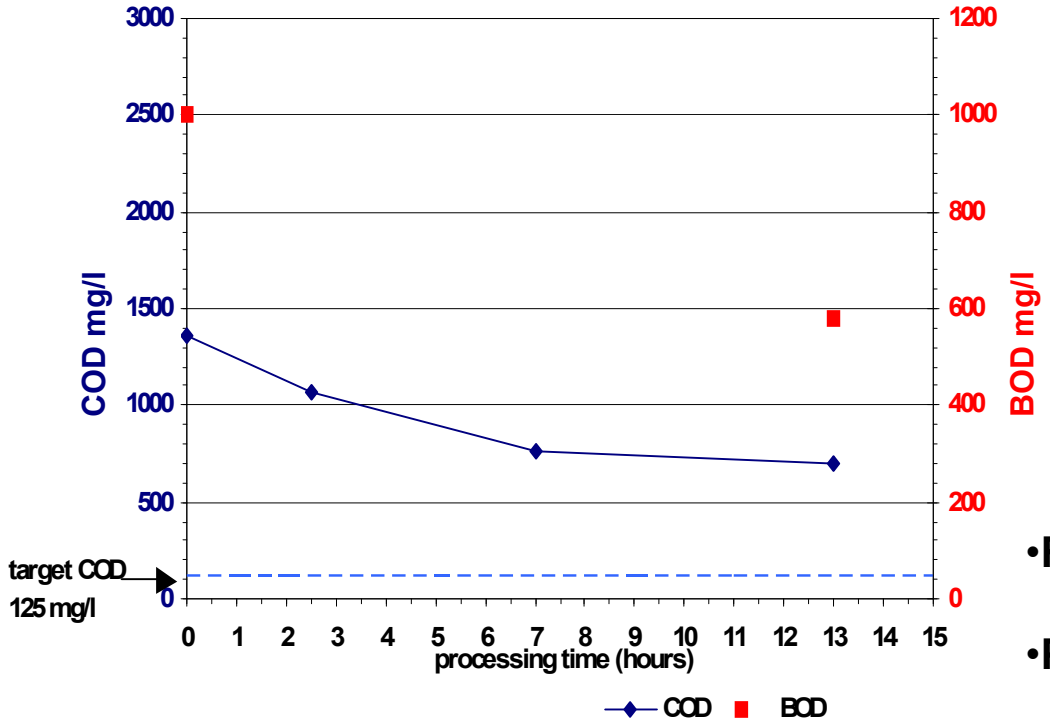
4 Tube Array
Processing graywater (continued)

- As expected 4 tube array processes volume of wastewater much faster
  - Time to reduce COD from 2500 to 1500 mg/ l is ~ 10 hours in single tube and less than 0.5 hour in 4 tube array

- COD decrease is non-linear with time. Most of the decrease occurs in the first few hours. Potential causes for plateau in performance:
  - Passivation of anode. Production of ferric oxide (rust) inhibits ferrate production
  - Recirculation of graywater has increasing concentration of ferric/ferrous ions. Possible interference in COD and BOD analysis.

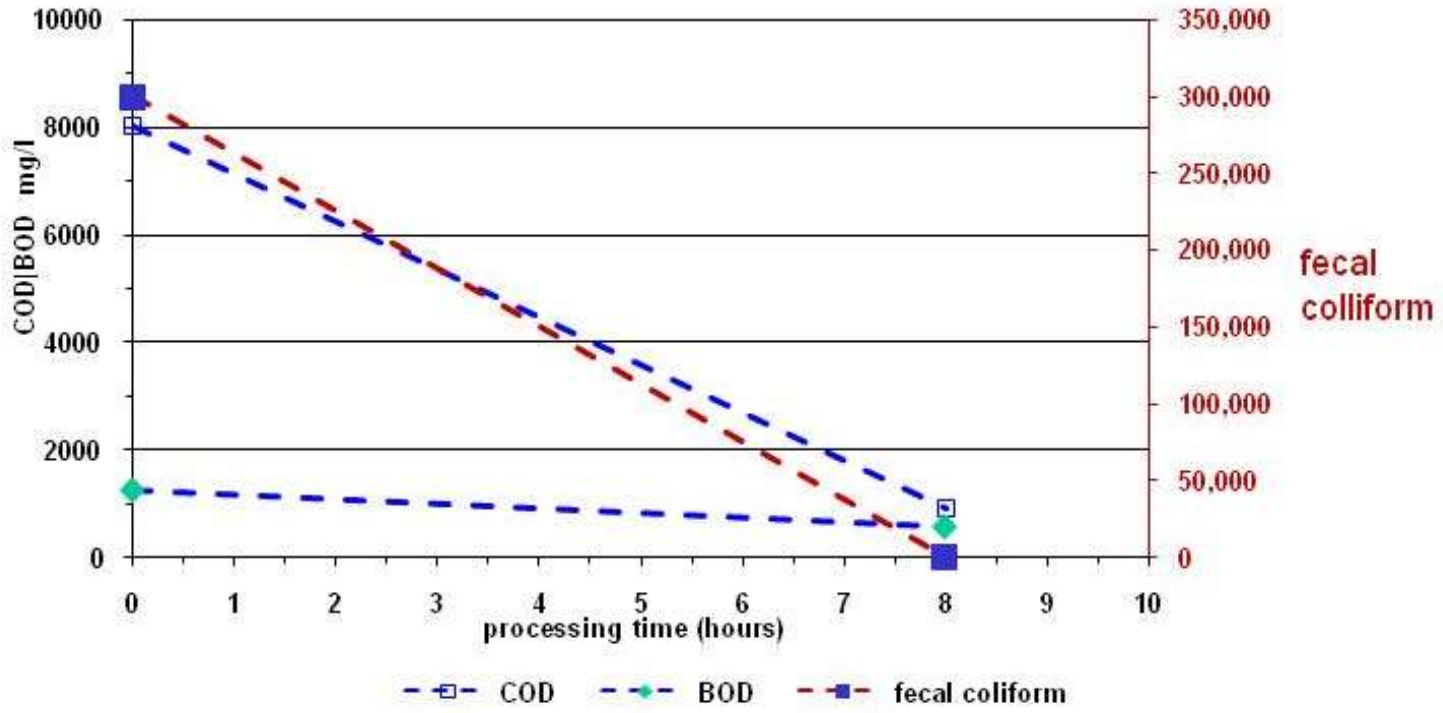
4 Tube Array
Processing 5 liters of graywater



- Replaced steel wool at 7 hour mark
- Plateau caused by interference from residual iron ions in sample?

Processing time scales with volume (factor of 8.3): In this test COD values drops from ~1500 to 700 in 8 hours compared to 600 ml test where the same drop occurred in less than 1 hour.

4 tube array
blackwater results



Volume:600 ml

Cell conditions: 2.7 V, 7.5 Amps

Wastewater sample: Lowell Regional wastewater facility Primary effluent

Ferrate Reactor Summary

- Demonstrated *in situ* production of ferrate in pH neutral wastewater

- Demonstrated decontamination of simulated graywater and blackwater
  - Best phase I results for graywater
    - 93% COD removal,
    - 70% BOD removal
  - Best phase I results for blackwater
    - 89 % COD removal,
    - 53% BOD removal
    - 98 % Fecal Coliform removal