In Situ Chemical Oxidation of Gasoline Compounds Using Persulfate

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In Situ Chemical Oxidation (ISCO)

Contemporary oxidants

- Potassium Permanganate ($KMnO_4$)
- Hydrogen Peroxide (H_2O_2)
- Sodium Persulfate ($Na_2S_2O_8$)

- Oxidant choice
  - Interaction with aquifer materials
  - Reactivity with organic compounds

Oxidant Choice

- MnO_4^- (Permanganate)
  - High TOC/reductant => High NOD
    - Unproductive oxidant consumption
  - Ineffective against PHCs etc.

Oxidant Choice

- H_2O_2 (Hydrogen Peroxide)
  - Enhanced decomposition rates
  - Limited radius of influence

Oxidant Choice

- $S_2O_8^{2-}$ (Persulfate)
  - Limited and contradictory literature
  - Complex oxidation/activation chemistry
    - Potentially complex interaction with aquifer materials on activation
    - Newest activation schemes
      - H_2O_2, High pH, Chelated Ferrous

Persulfate

– High oxidation potential on activation (E^o = 2.6 V)

– Potentially widespread reactivity

– High aqueous solubility (~550 g/L)

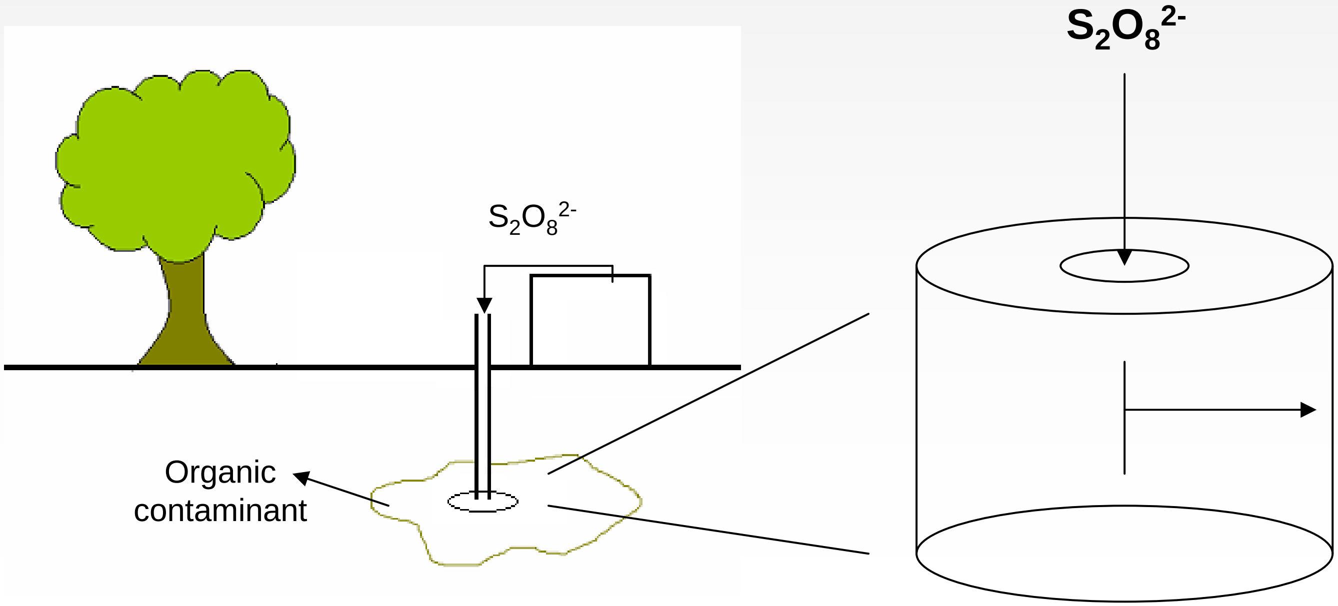
ISCO Applications

Understanding Persulfate

- Persistence in aquifer media
  - Activation strategies: Natural, H_2O_2, Fe(II), pH
- Oxidation of prevalent target organics (PHCs)

Objective 1: Persistence

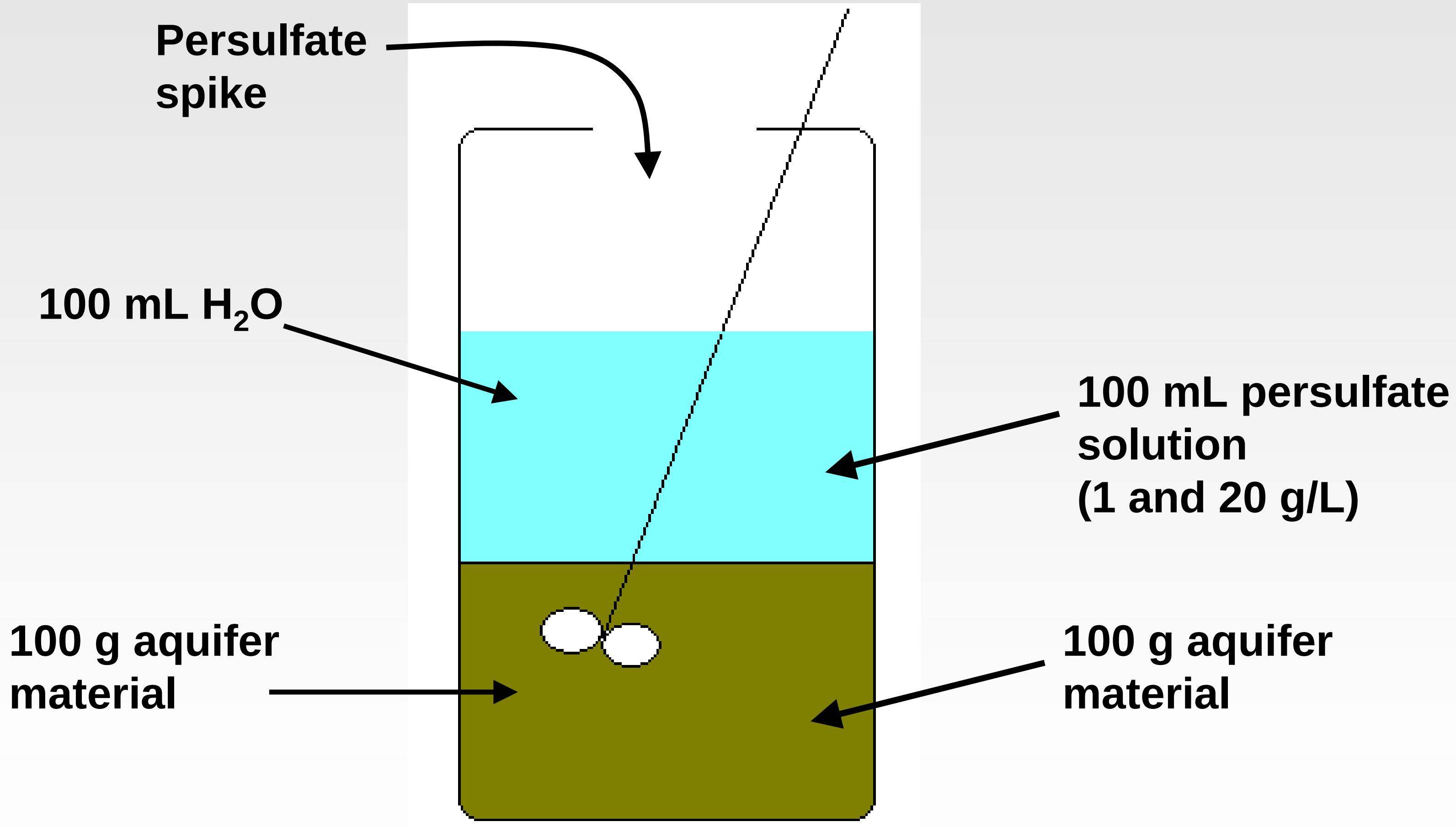
- Function of
  - Auto-decomposition
  - Reactions with non-target chemicals in soil
  - Interaction with activating agents



Overview of Investigations

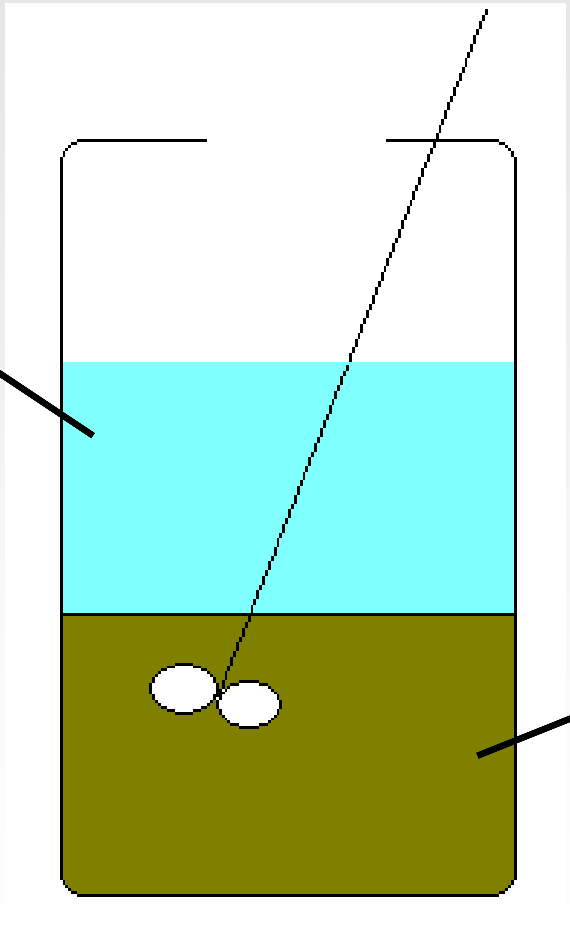
- Bench-scale (7 aquifer materials)
  - Batch Tests (1 and 20 g/L)
  - Column Tests
- Pilot-scale (CFB Borden)
  - Push-Pull Tests

Batch Reactor



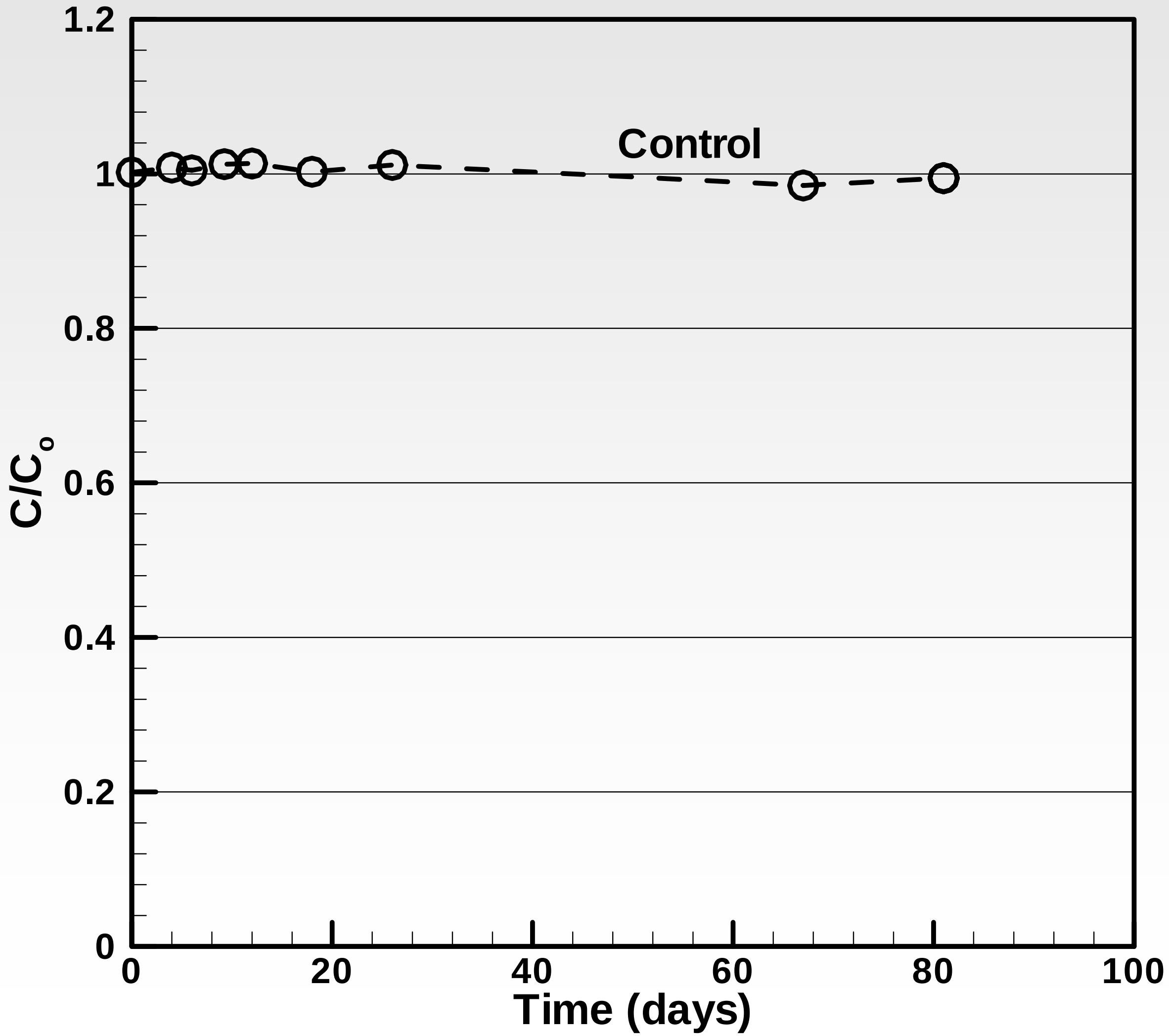
Batch Tests

Temporal sampling for persulfate, pH

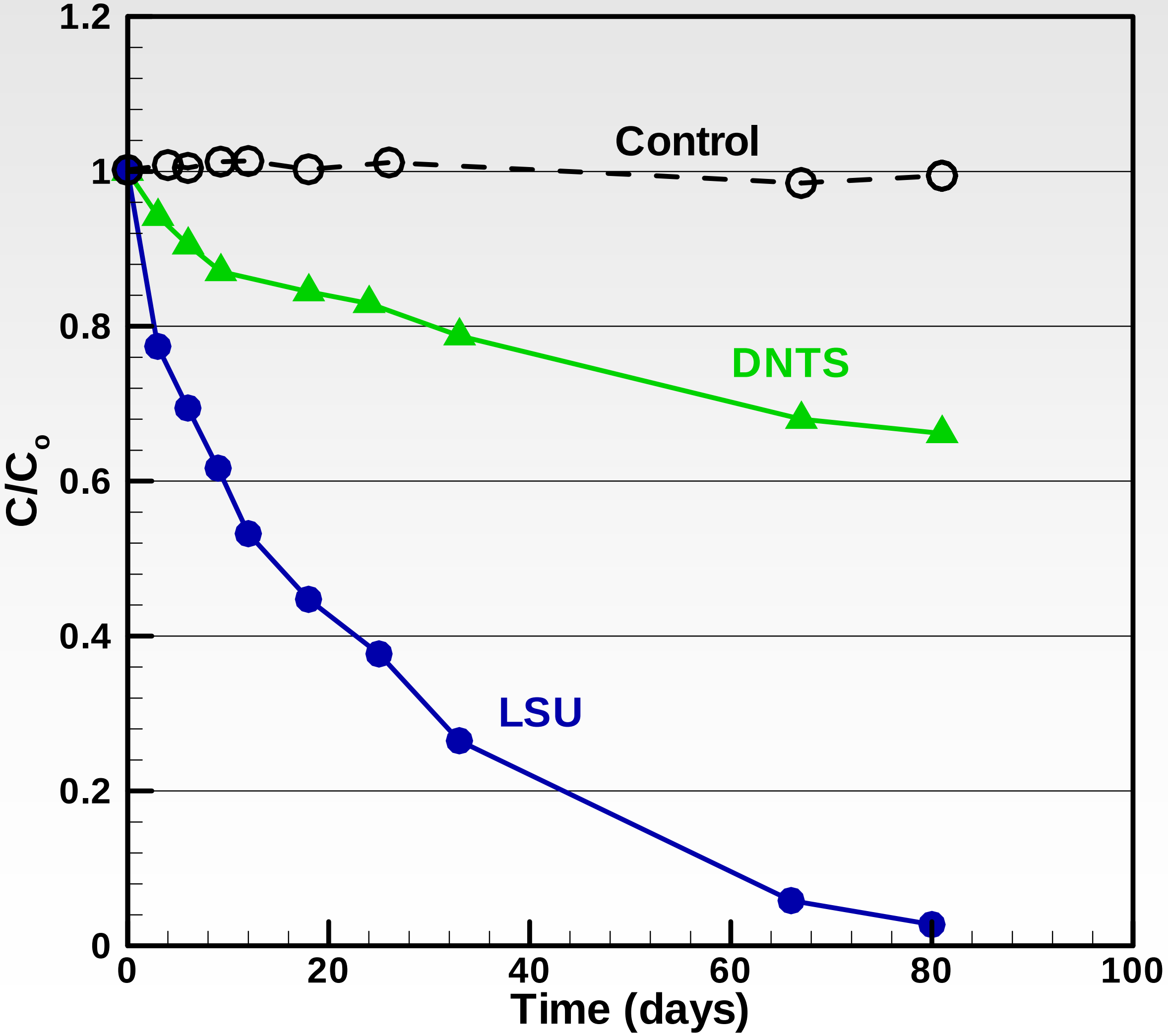


Pre and post-oxidation analyses for COD

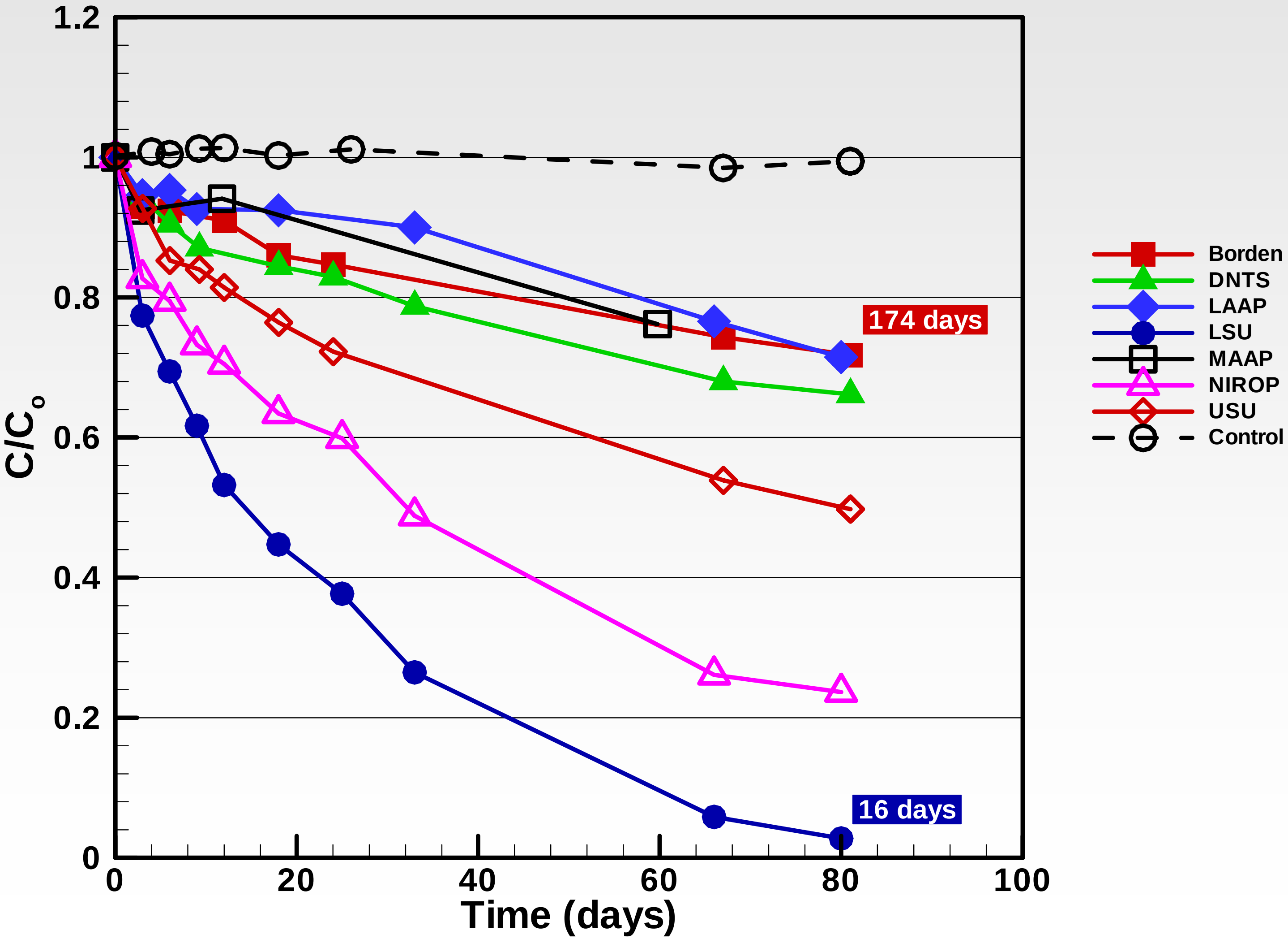
Batch Results (1 g/L)



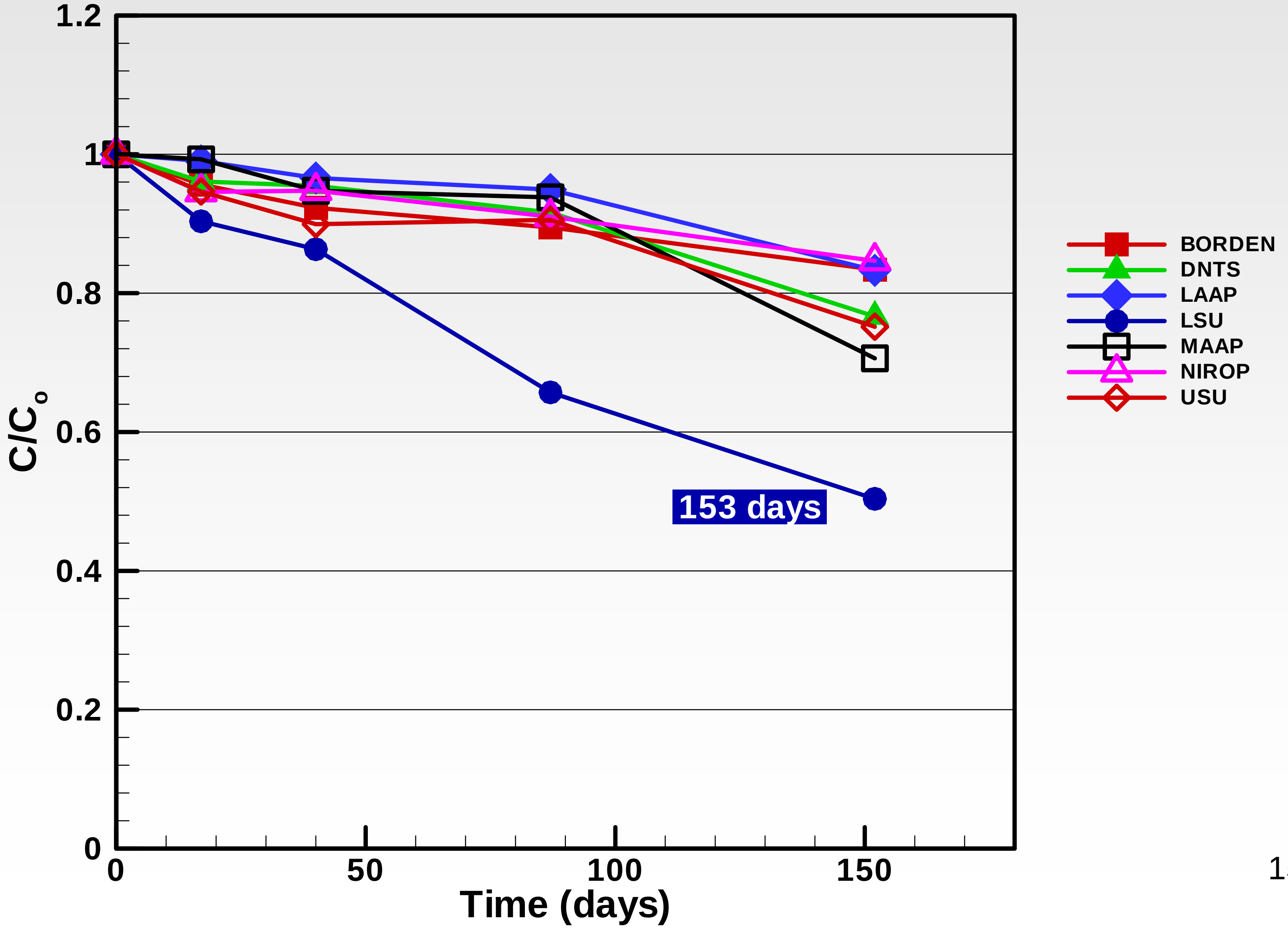
Batch Results (1 g/L)



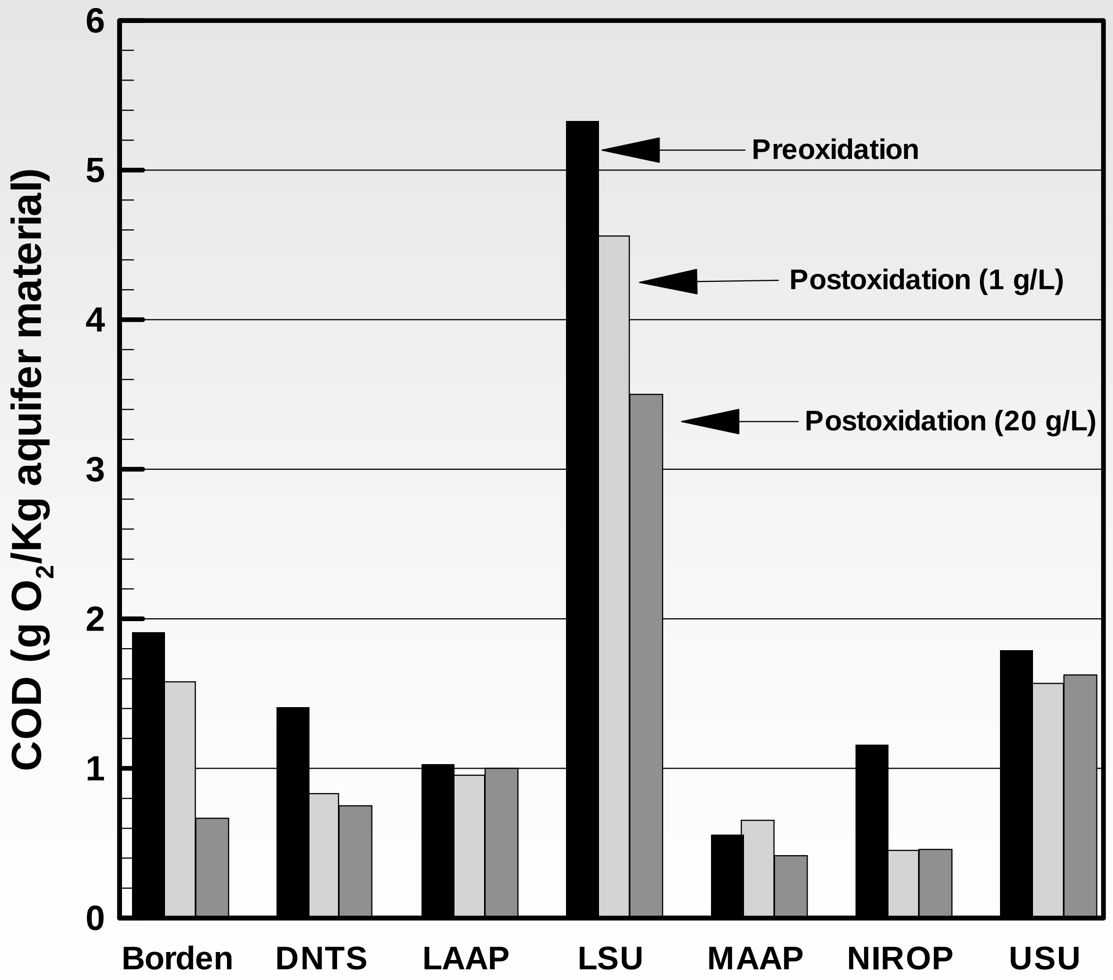
Batch Results (1 g/L)



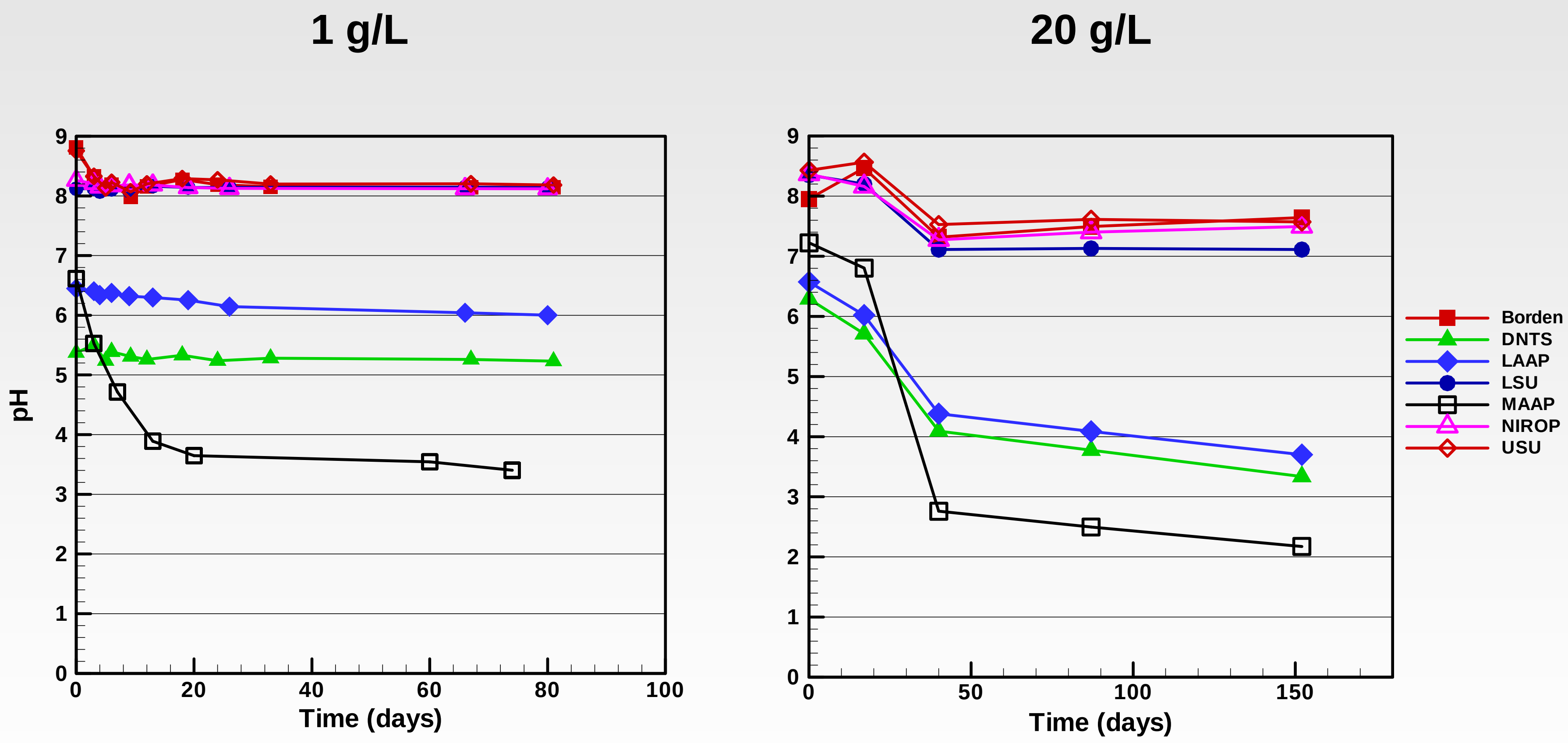
Batch Results (20 g/L)



COD Reduction



Effect on pH



1 g/L
20 g/L
pH
Time (days)
Time (days)
Borden
DNTS
LAAP
LSU
MAAP
NIROP
USU

Summary of kinetic data

Aquifer Material	Half-life, $t_{1/2}$ (days)	
	1 g/L	20 g/L
Borden	174	515
DNTS	117	396
LAAP	185	548
LSU	16	153
MAAP	188	303
NIROP	36	454
USU	78	391

Degradation Rate Controlling Factors

<u>1 g/L</u>

- k_{obs} = f (TOC,Fe-Amor)
- $R^2 = 0.92$

<u>20 g/L</u>

- k_{obs} = f (COD)
- $R^2 = 0.95$

- Concentration of persulfate
- Exposure time
- Dissolution and exposure of minerals due to H^+ production

Objective 2: Treatability of Gasoline

- To evaluate utility of persulfate in treatment of gasoline compounds i.e.
  - Effectiveness at two persulfate concentrations
  - Effectiveness and efficiency using different persulfate activation strategies
    - Chelated Fe(II)
    - H_2O_2
    - Natural (aquifer materials)

Gasoline compounds

- Prevalence, persistence and toxicity
  - Benzene, Toluene, Ethylbenzene, Xylenes (BTEX)
  - Trimethylbenzenes (TMBs)
  - Naphthalene

- Petroleum hydrocarbon fractions
  - F1 (C_6 – C_{10})
  - F2 (C_{10} – C_{16})
  - TPH (Total Petroleum Hydrocarbons)

Treatments

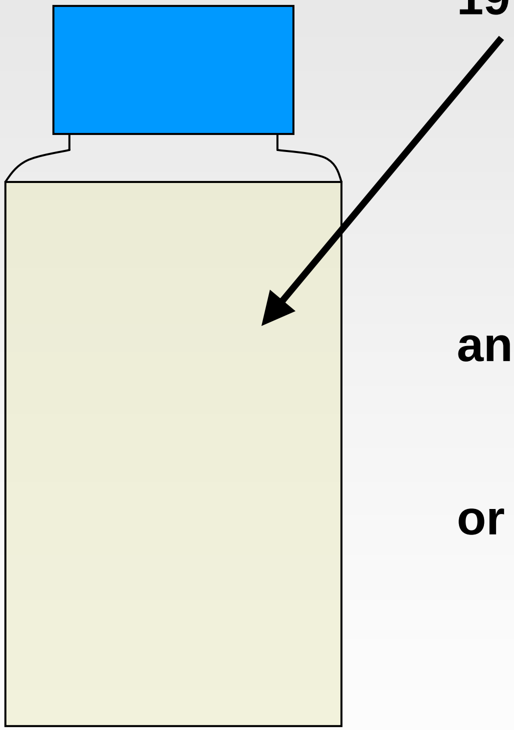
API Standard Gasoline @ ~25 mg/L

- Control

- Unactivated System
  - 1 or 20 g/L Persulfate

- Activated System @ 20 g/L Persulfate
  - Peroxide
    - 0.1 or 1.0 mol H_2O_2/mol $S_2O_8^{2-}$
  - Chelated Fe (II) (w/ Citric acid 1:1 molar ratio)
    - 150 or 600 mg/L Fe(II)
  - Natural
    - Two aquifer materials: Borden, LSU

Batch Reactor Systems (Aqueous)



19 mL aqueous solution

- **Gasoline ~25 mg/L**

- **Persulfate @ 1 or 20 g/L**

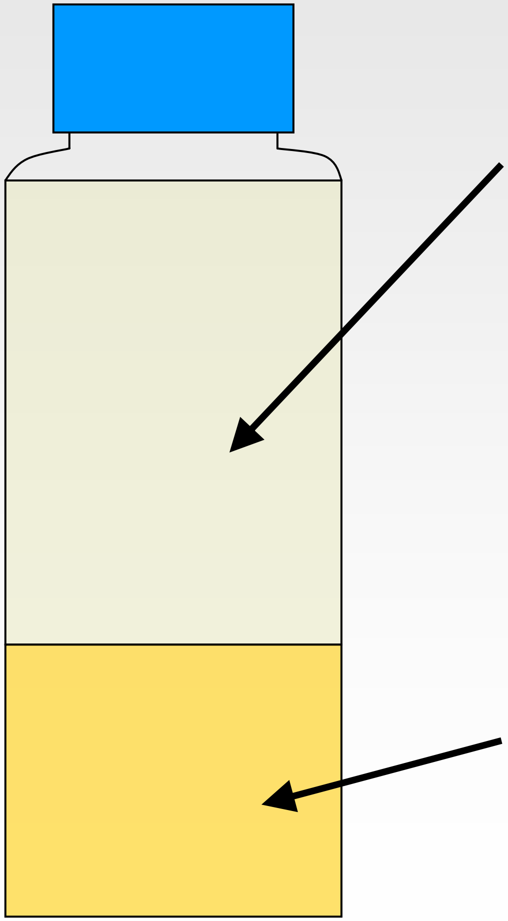
and

- **Peroxide – 0.1 or 1.0 mol H_2O_2/mol $S_2O_8^{2-}$**

or

- **Chelated Fe(II) – 150 or 600 mg/L**

Batch Reactor Systems (Solids)



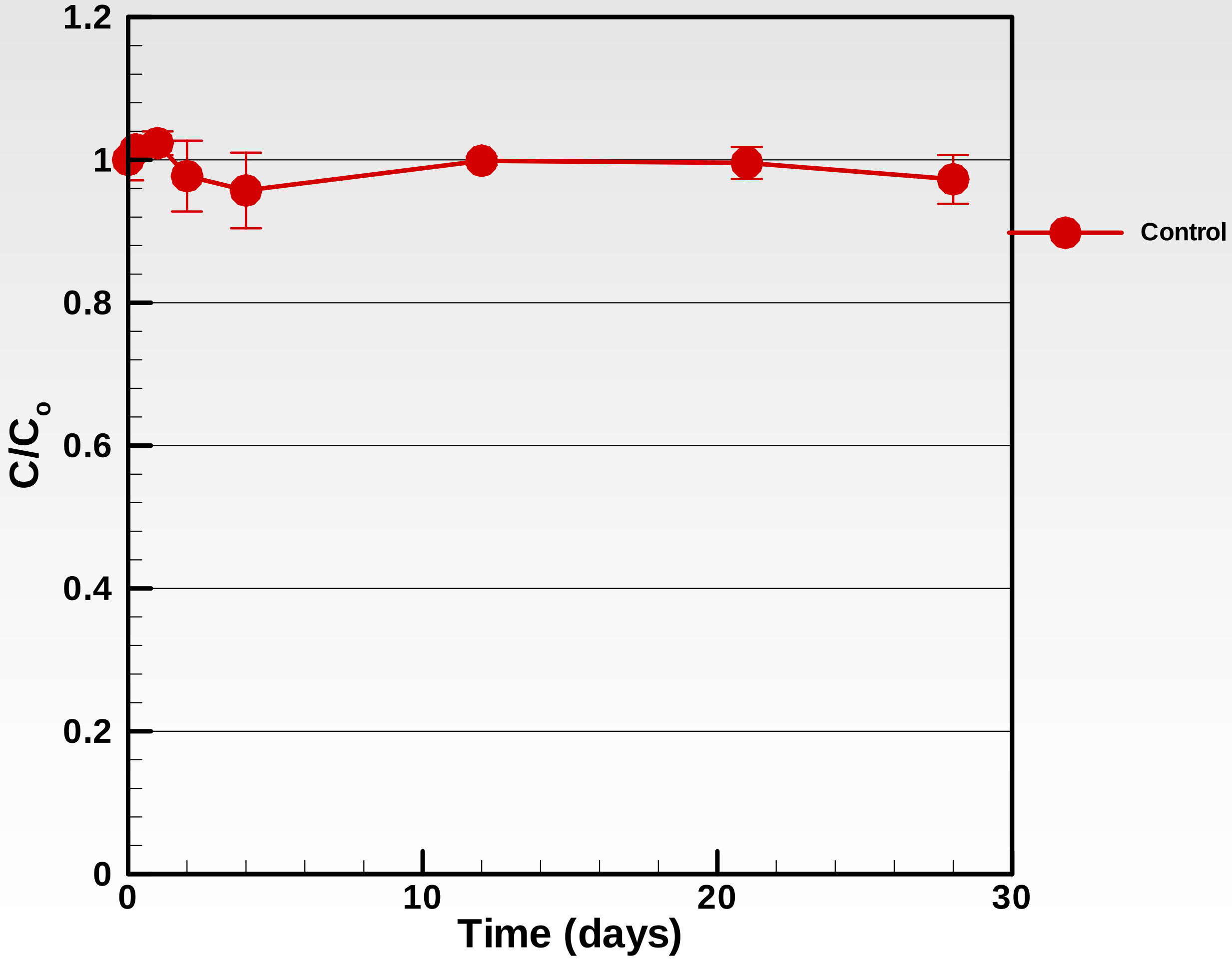
30 mL aqueous solution

- **Gasoline ~25 mg/L**
- **Persulfate @ 20 g/L**

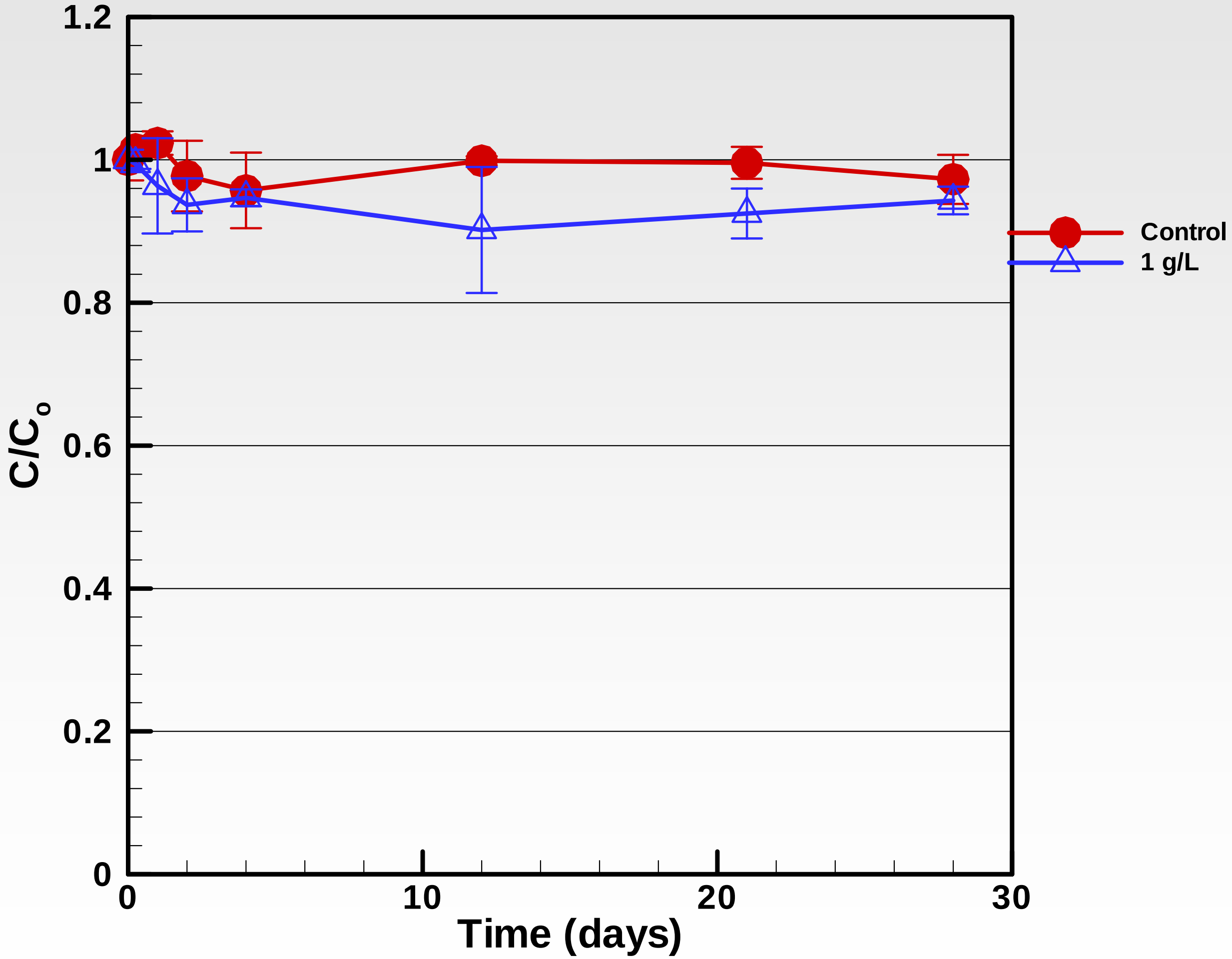
30 g soil mass

- **Borden or LSU-LC34**

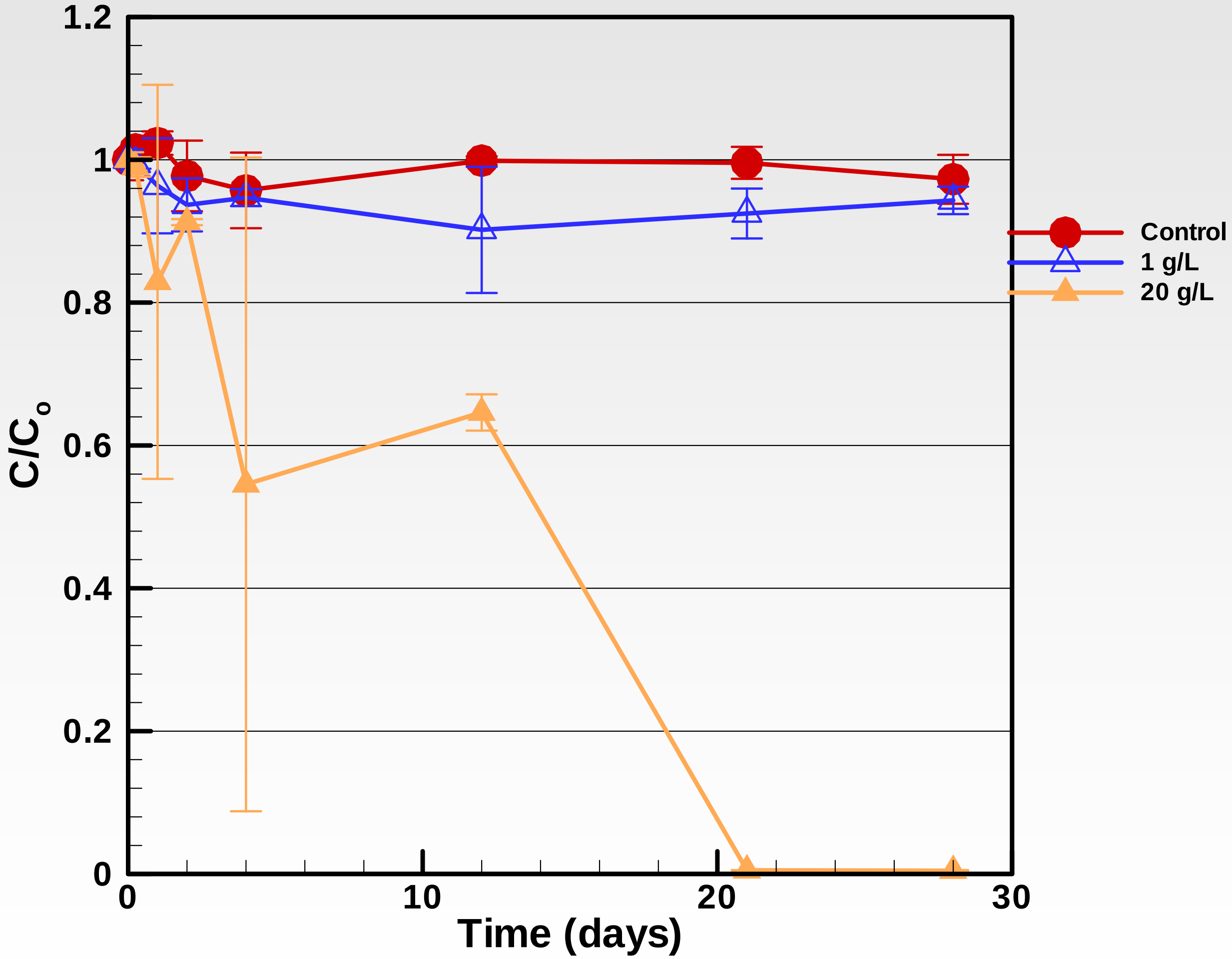
Benzene Results



Benzene Results



Benzene Results



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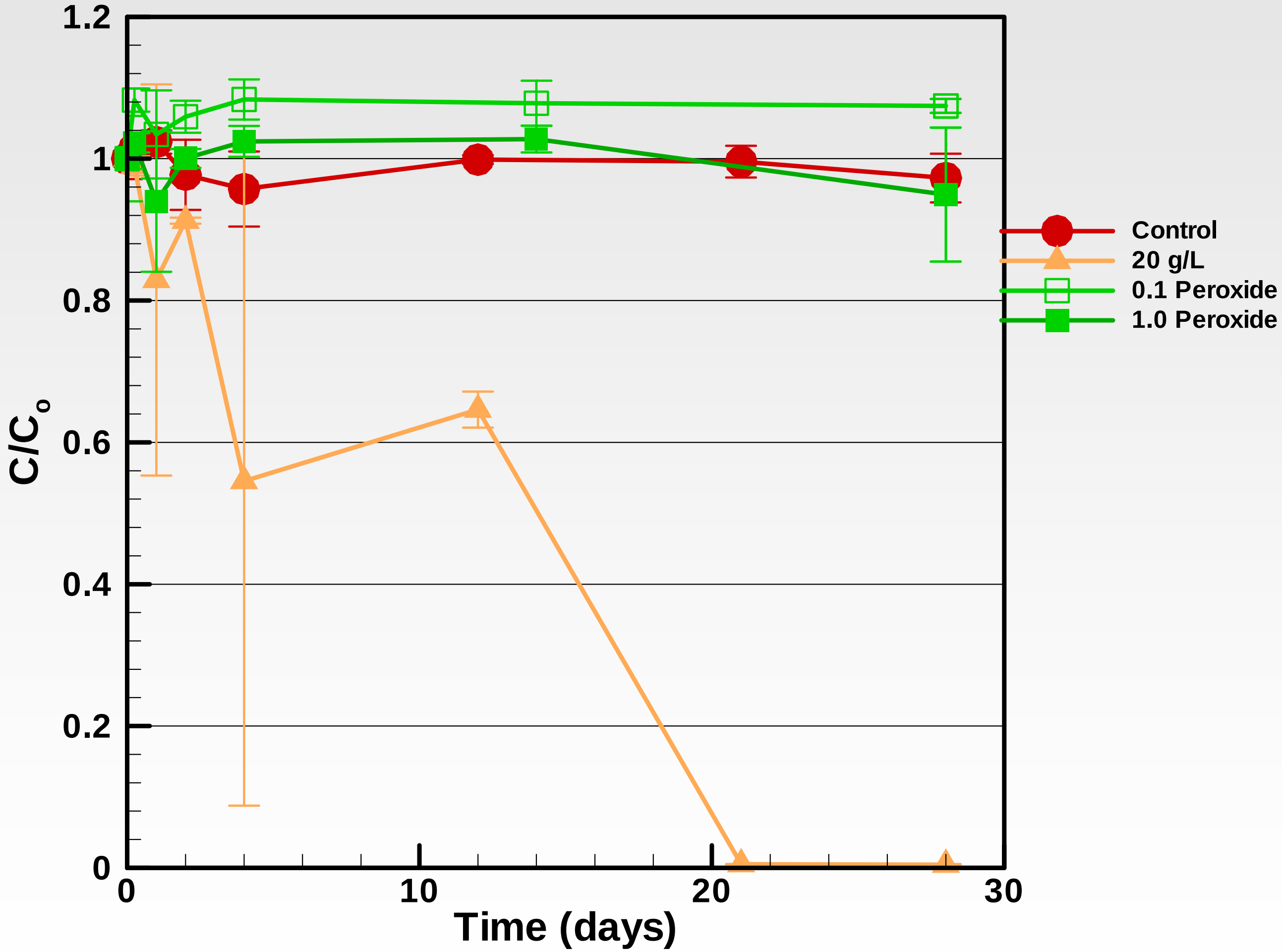

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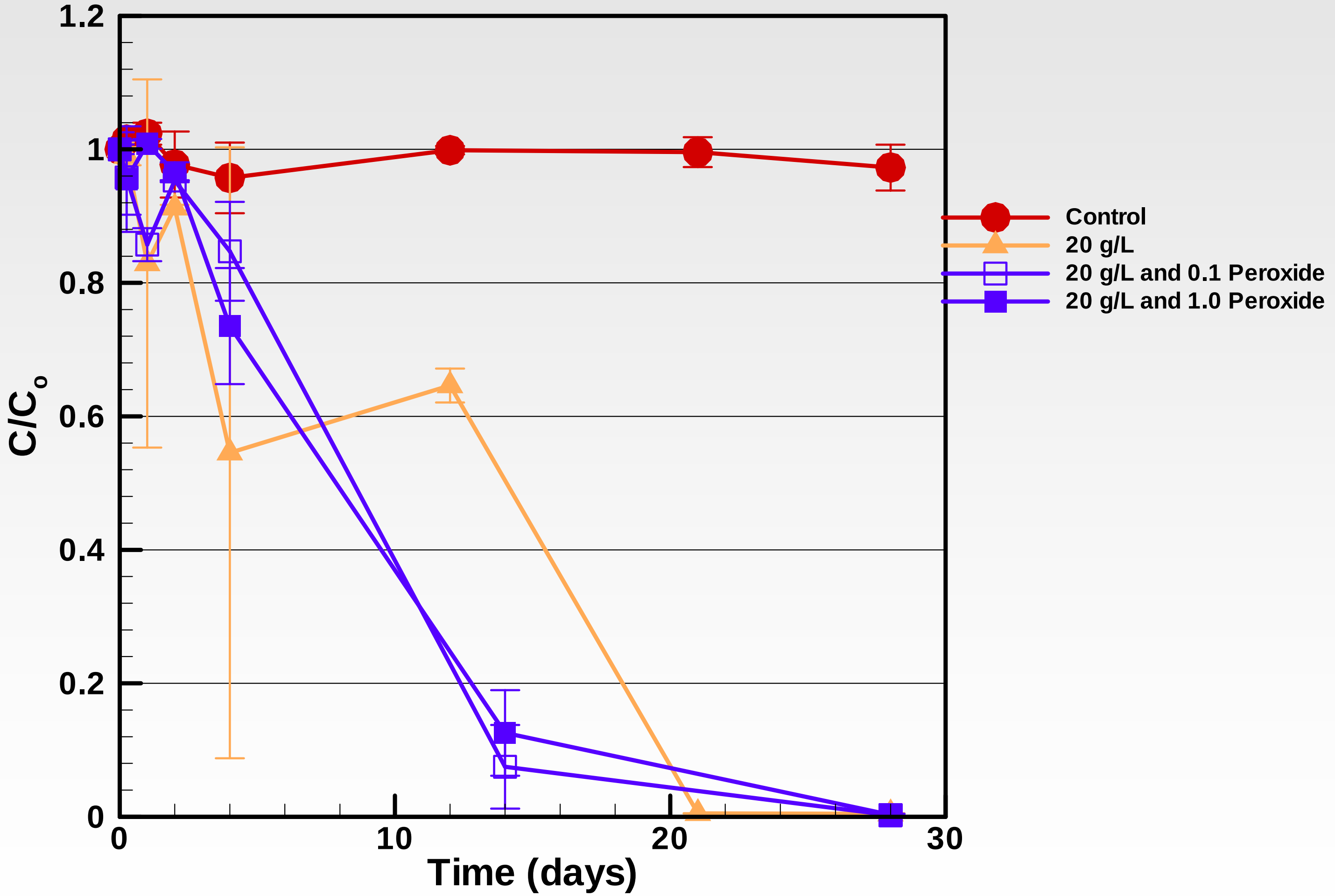

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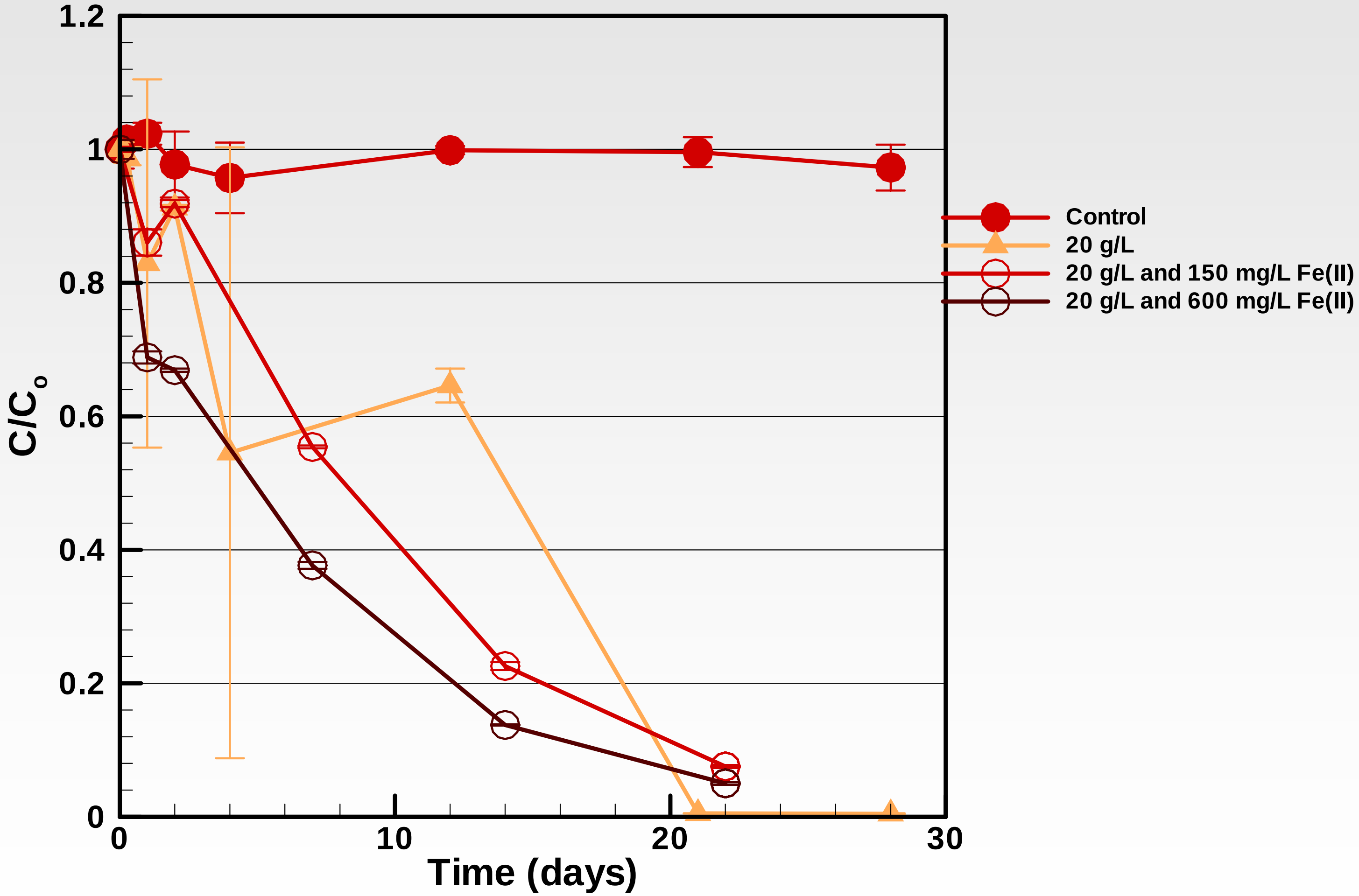

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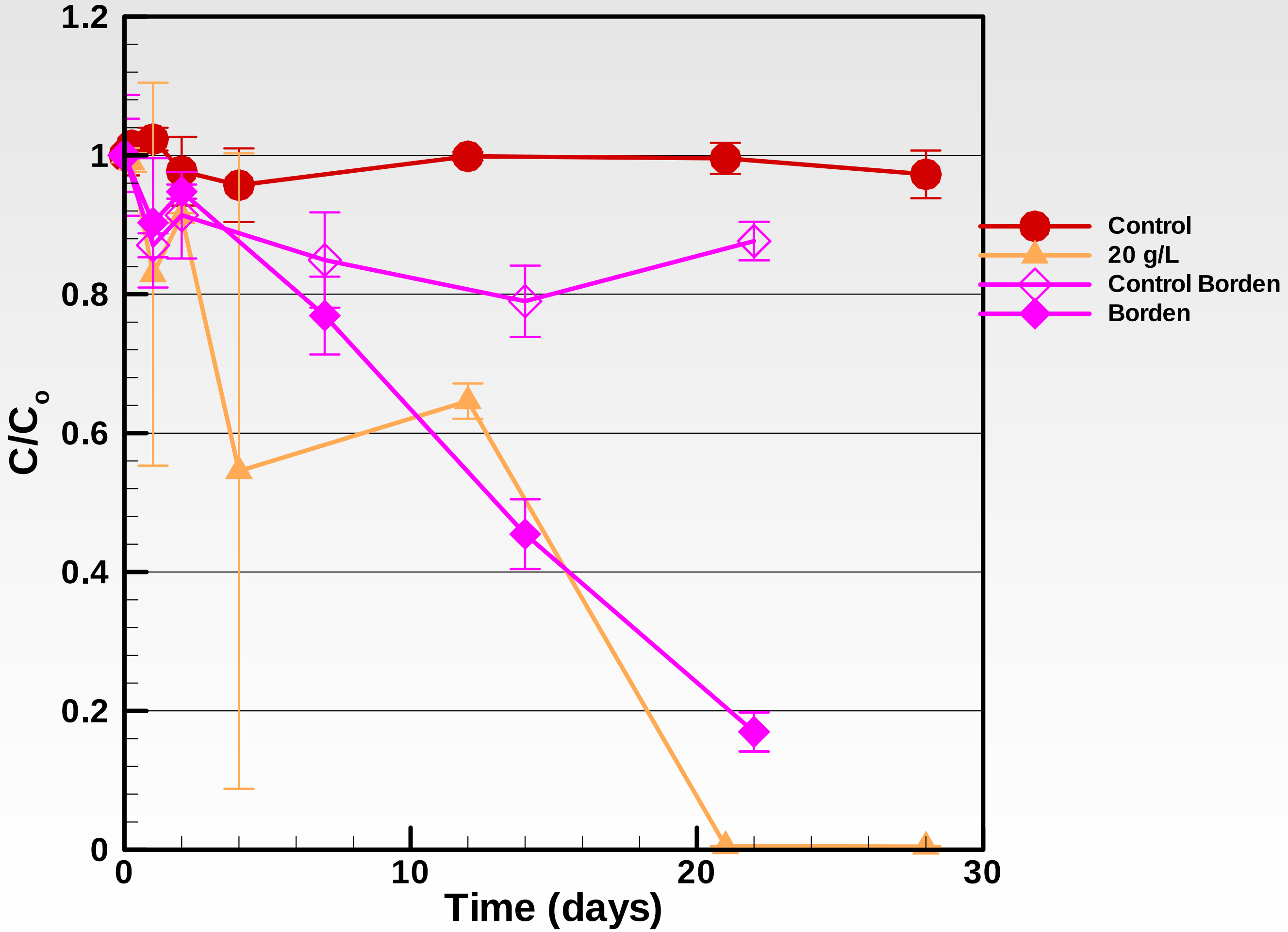

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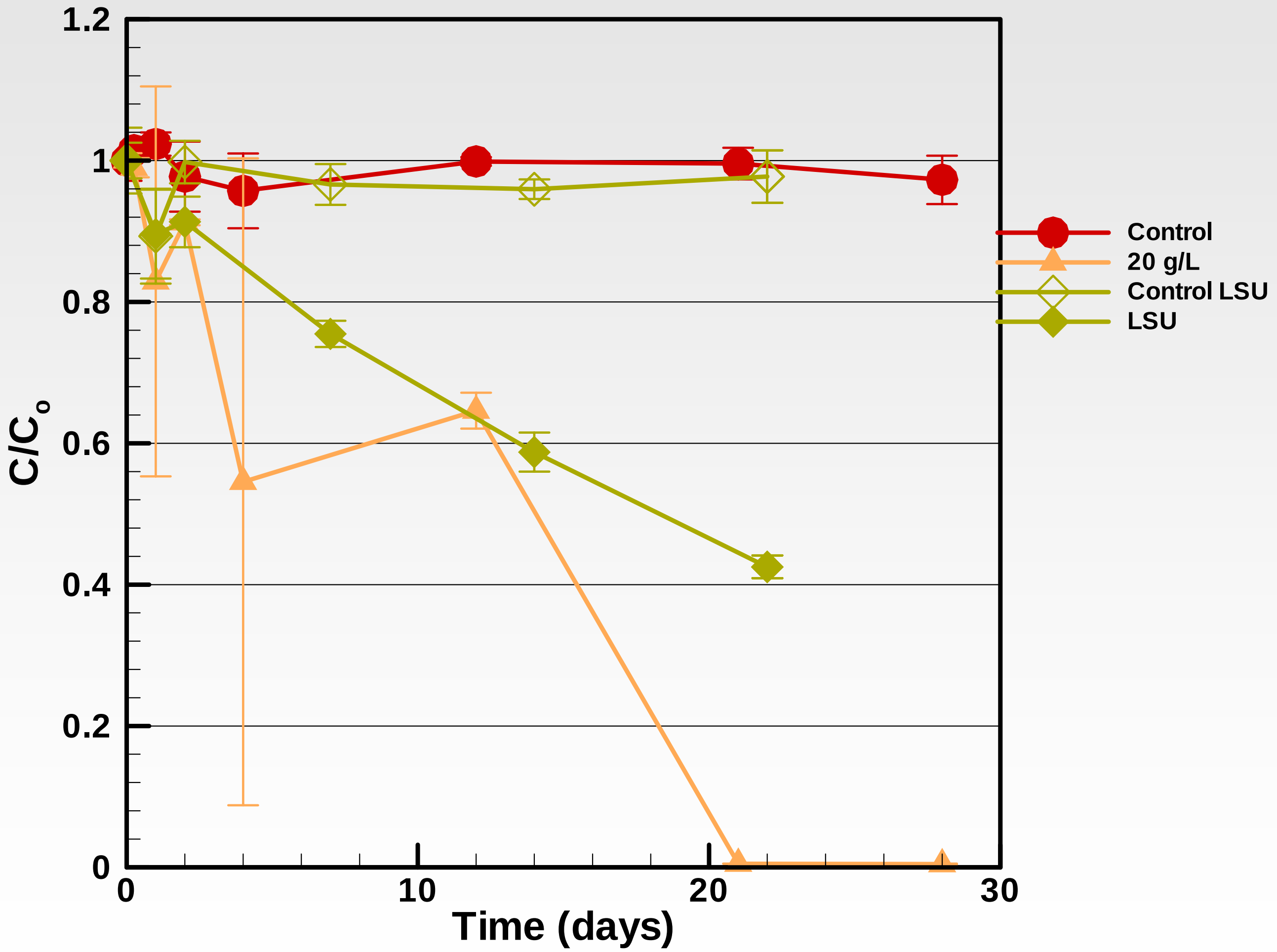

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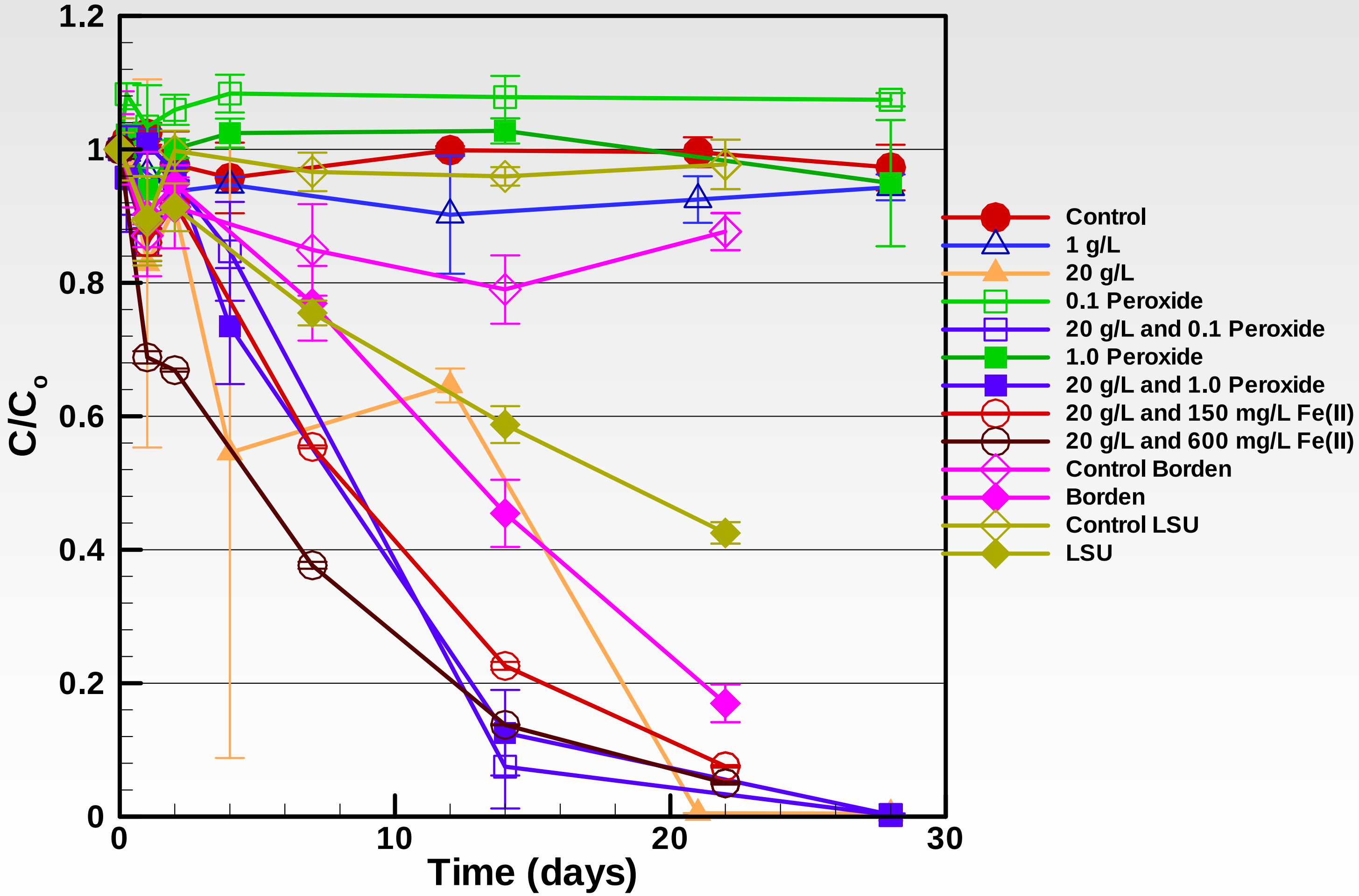

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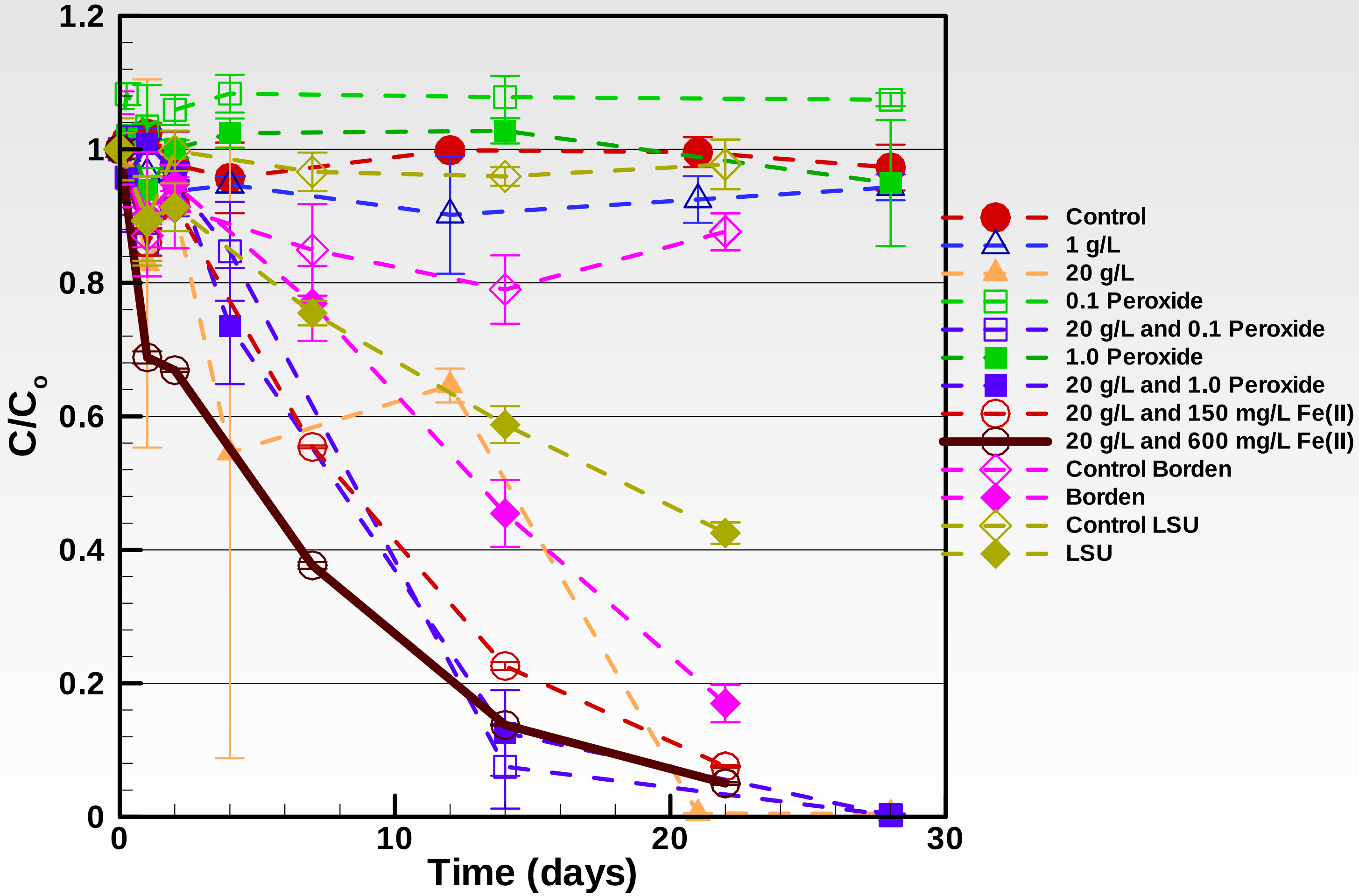

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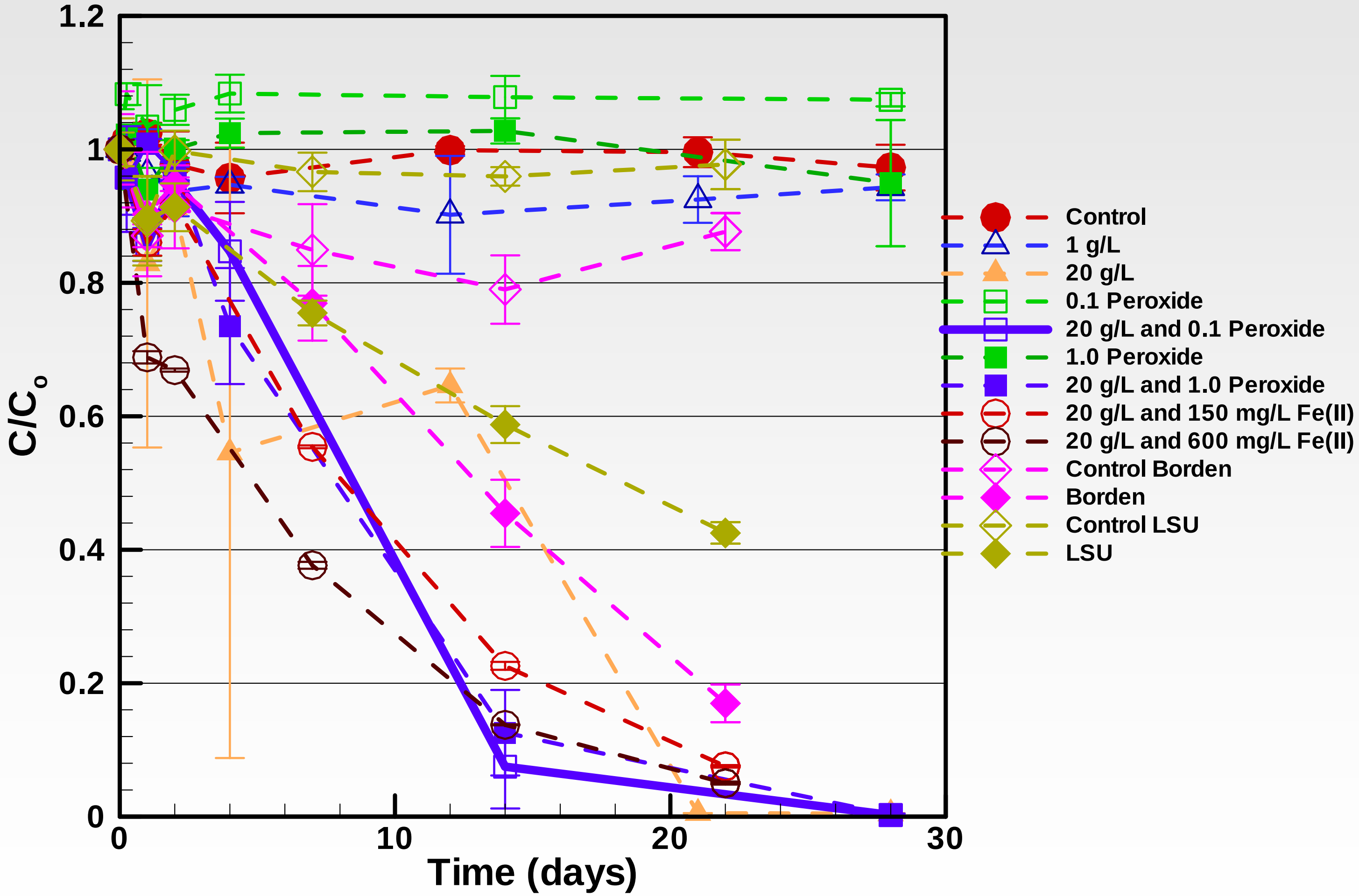

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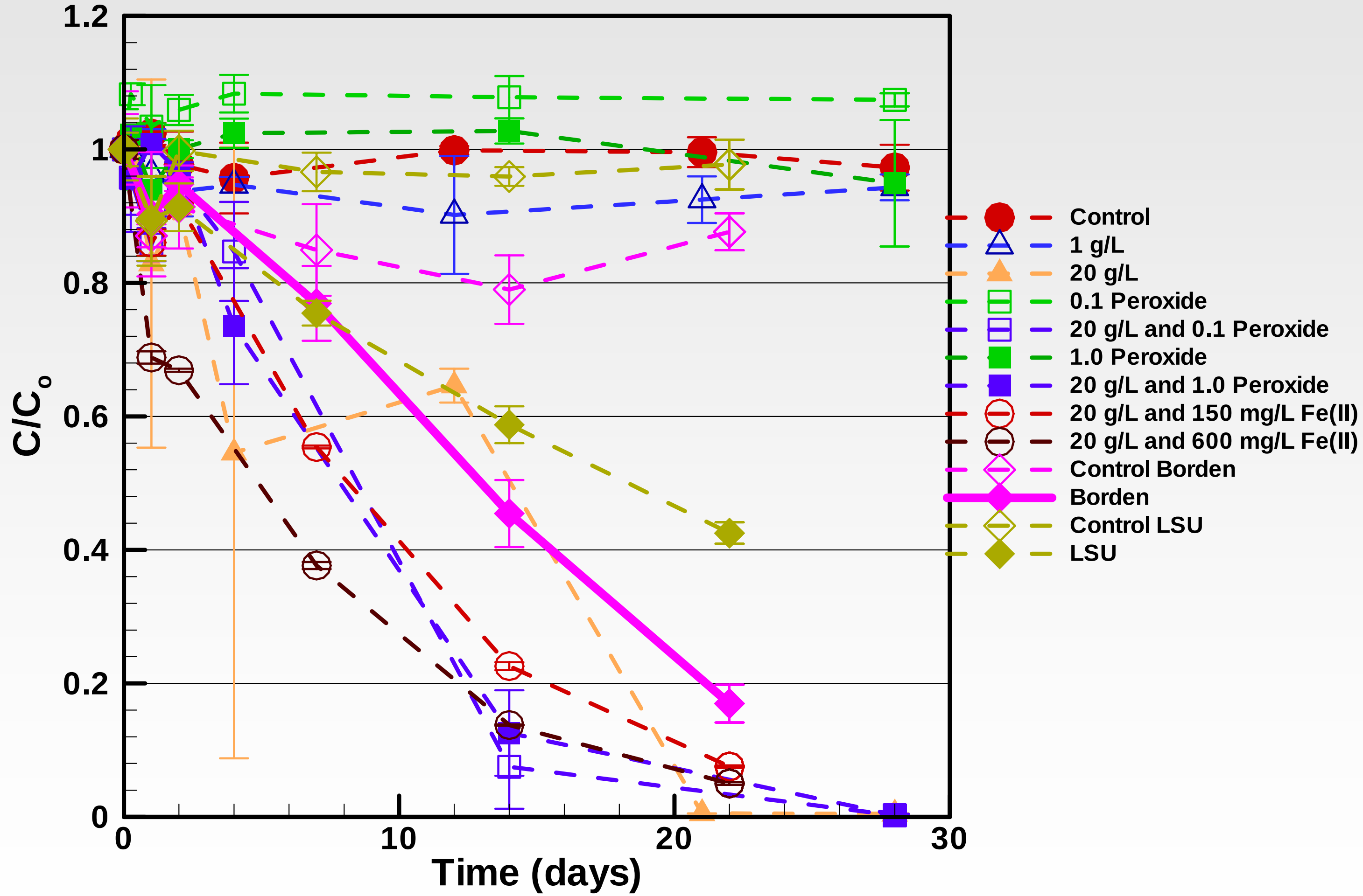
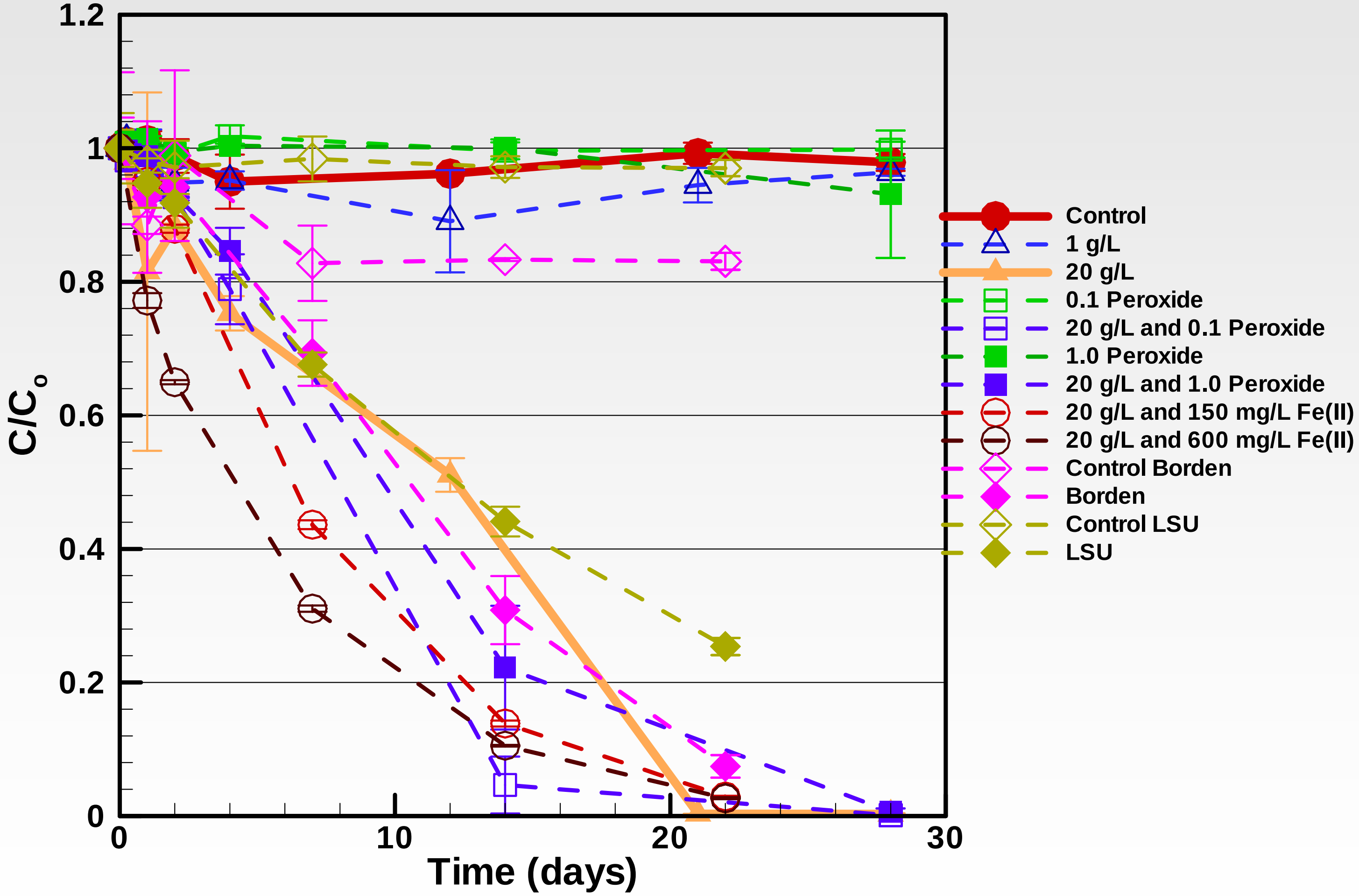


Toluene Results



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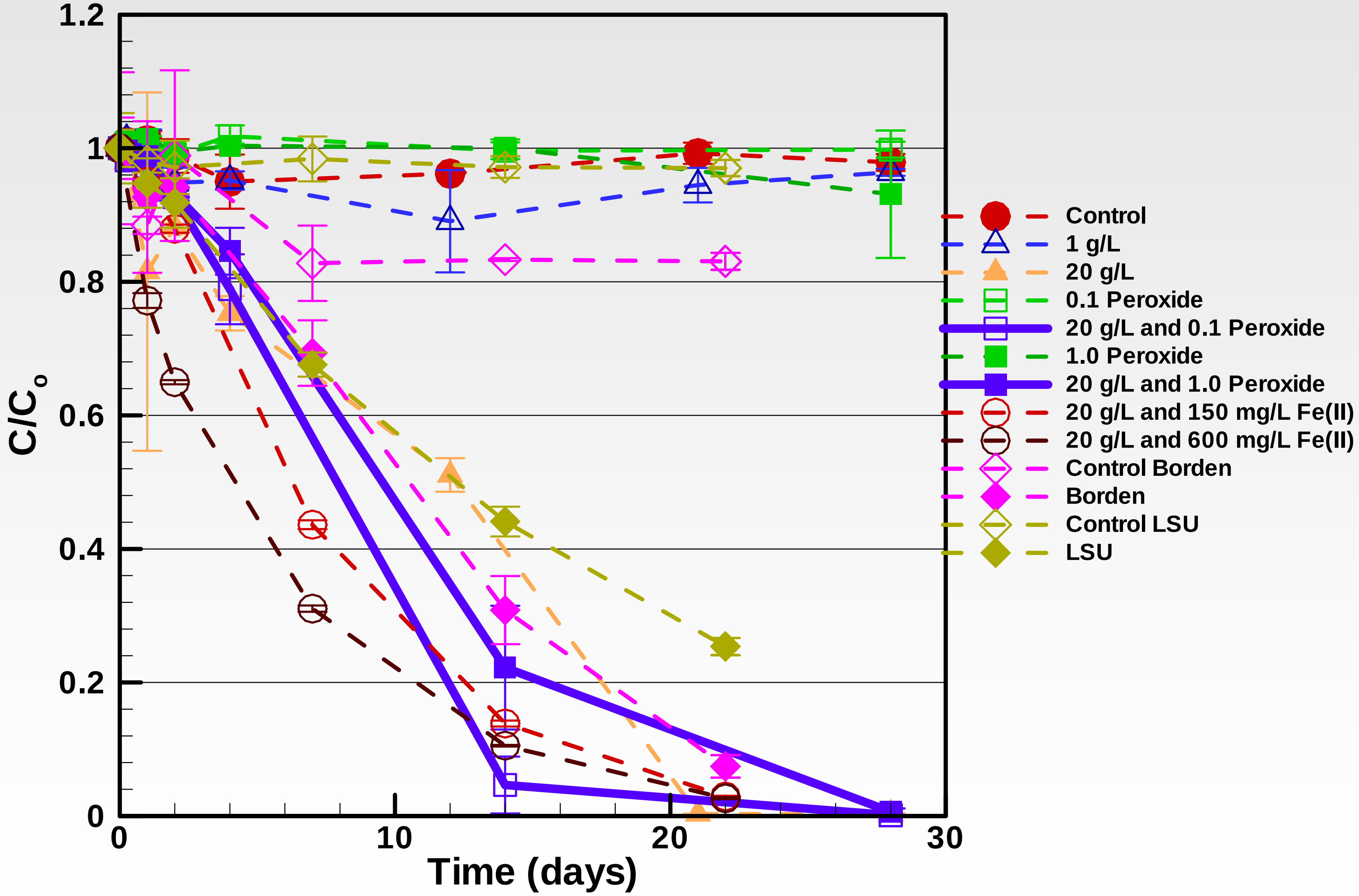

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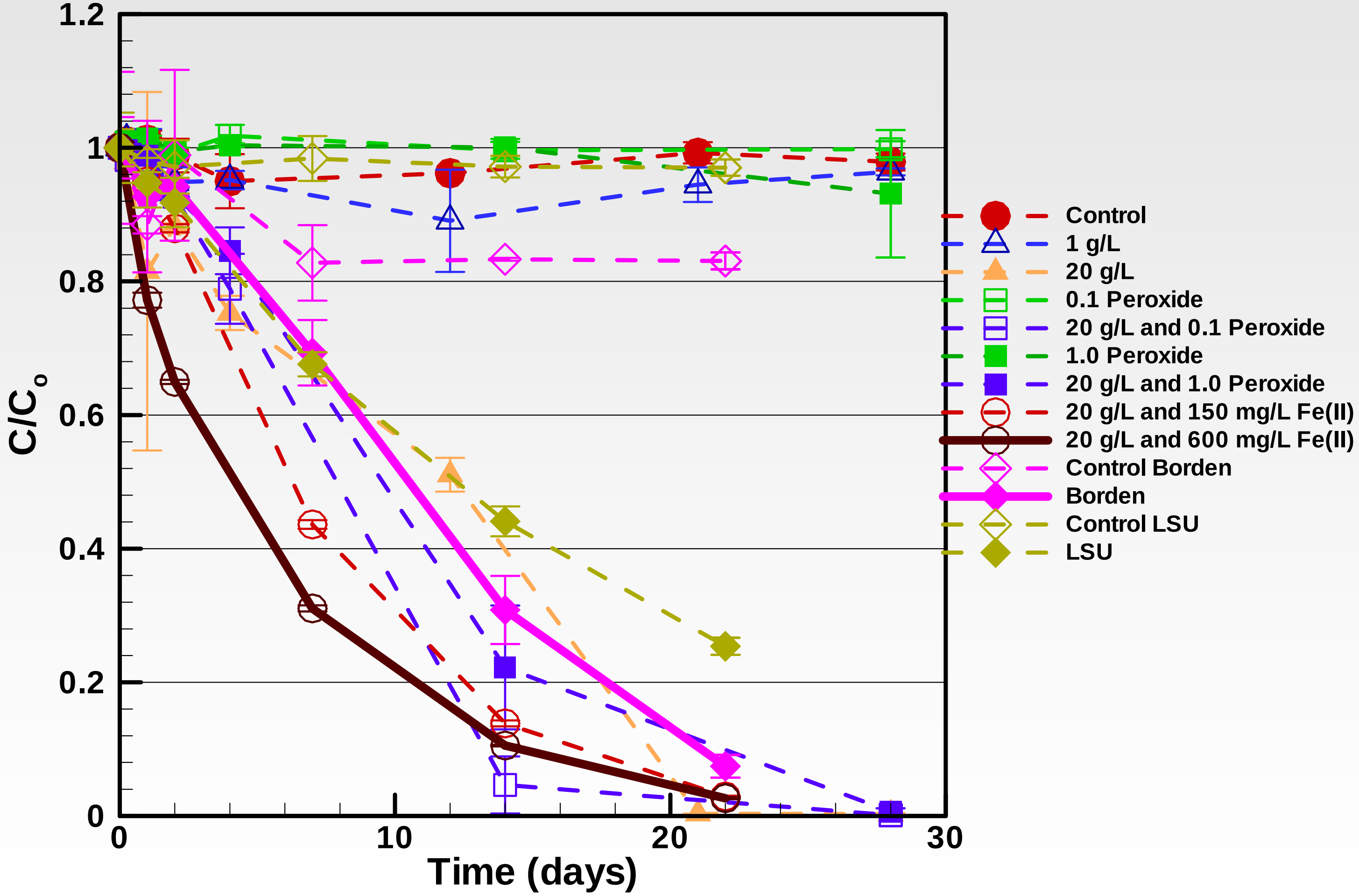
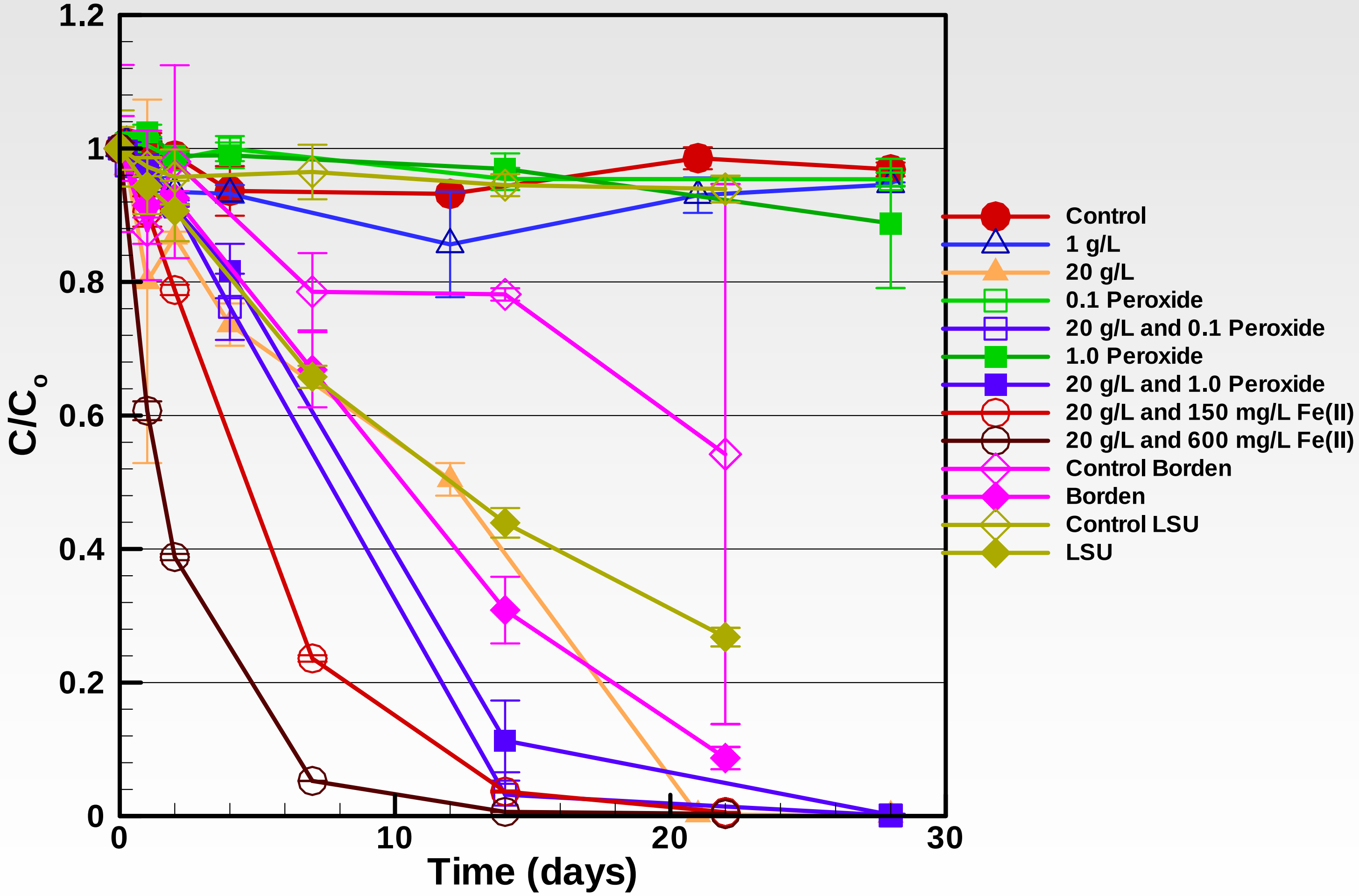
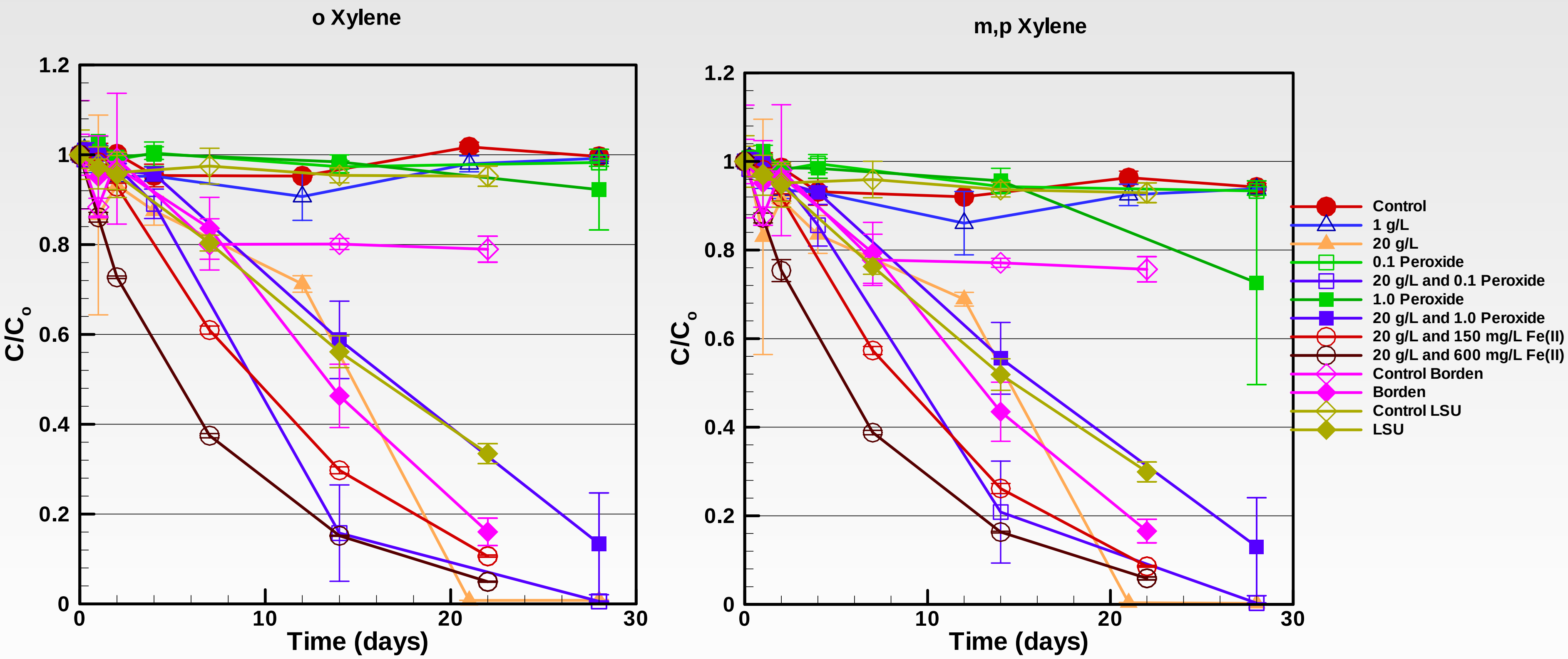


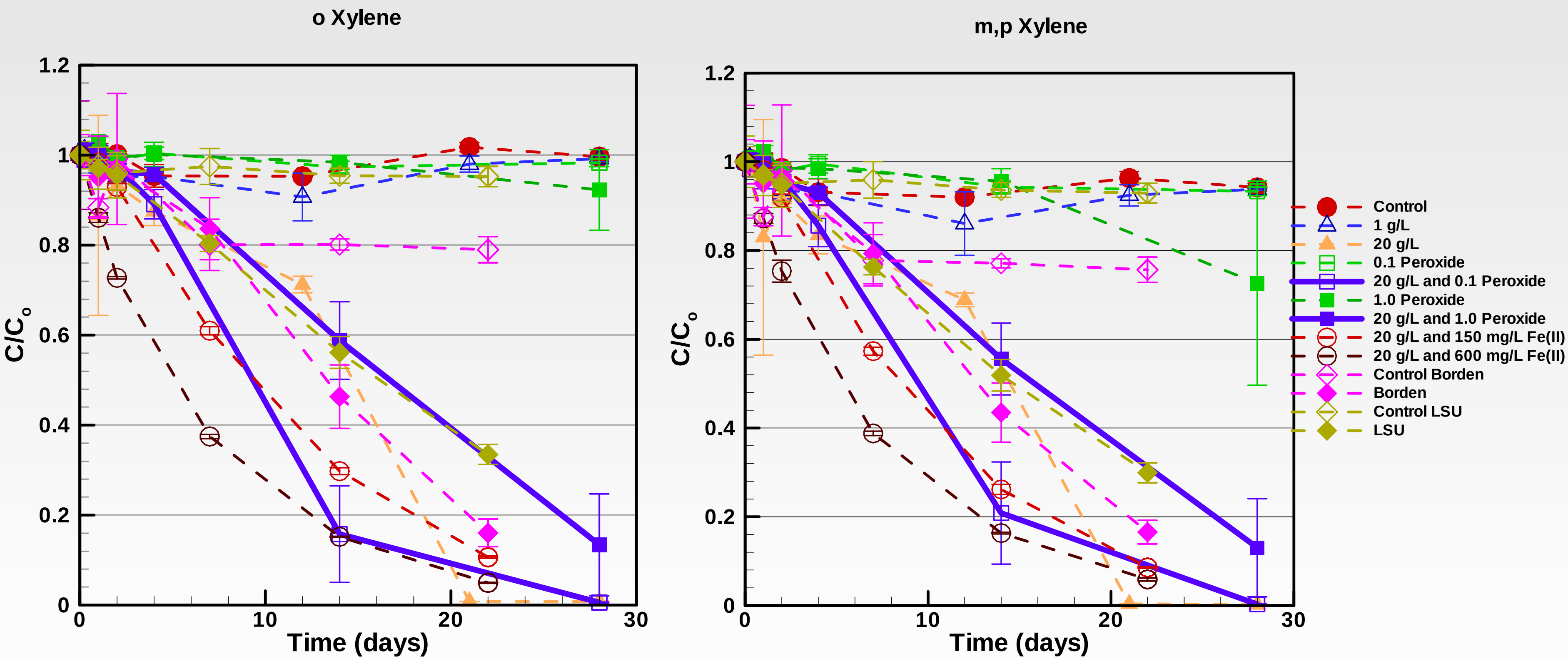
Ethylbenzene Results



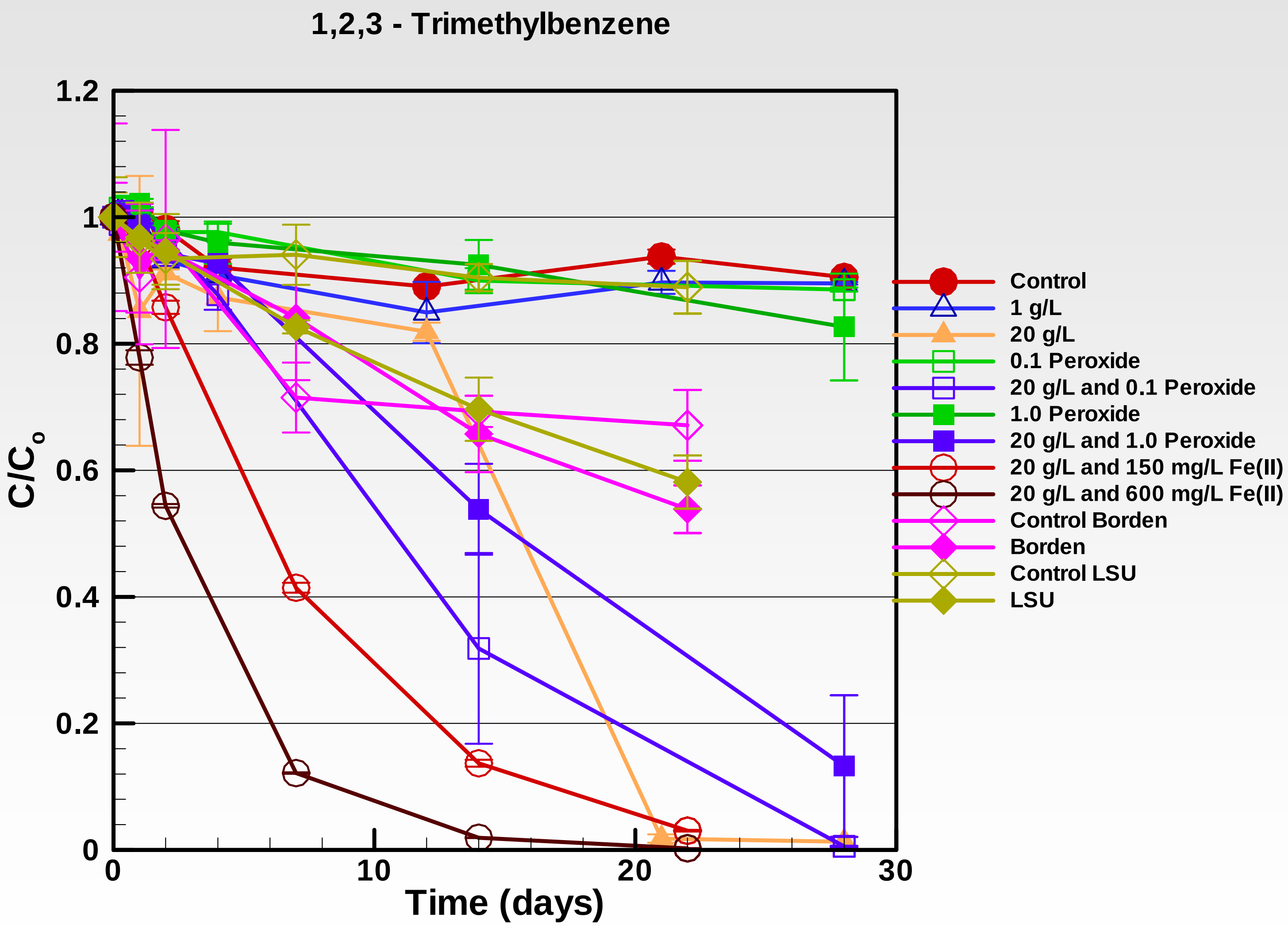
Xylenes Results



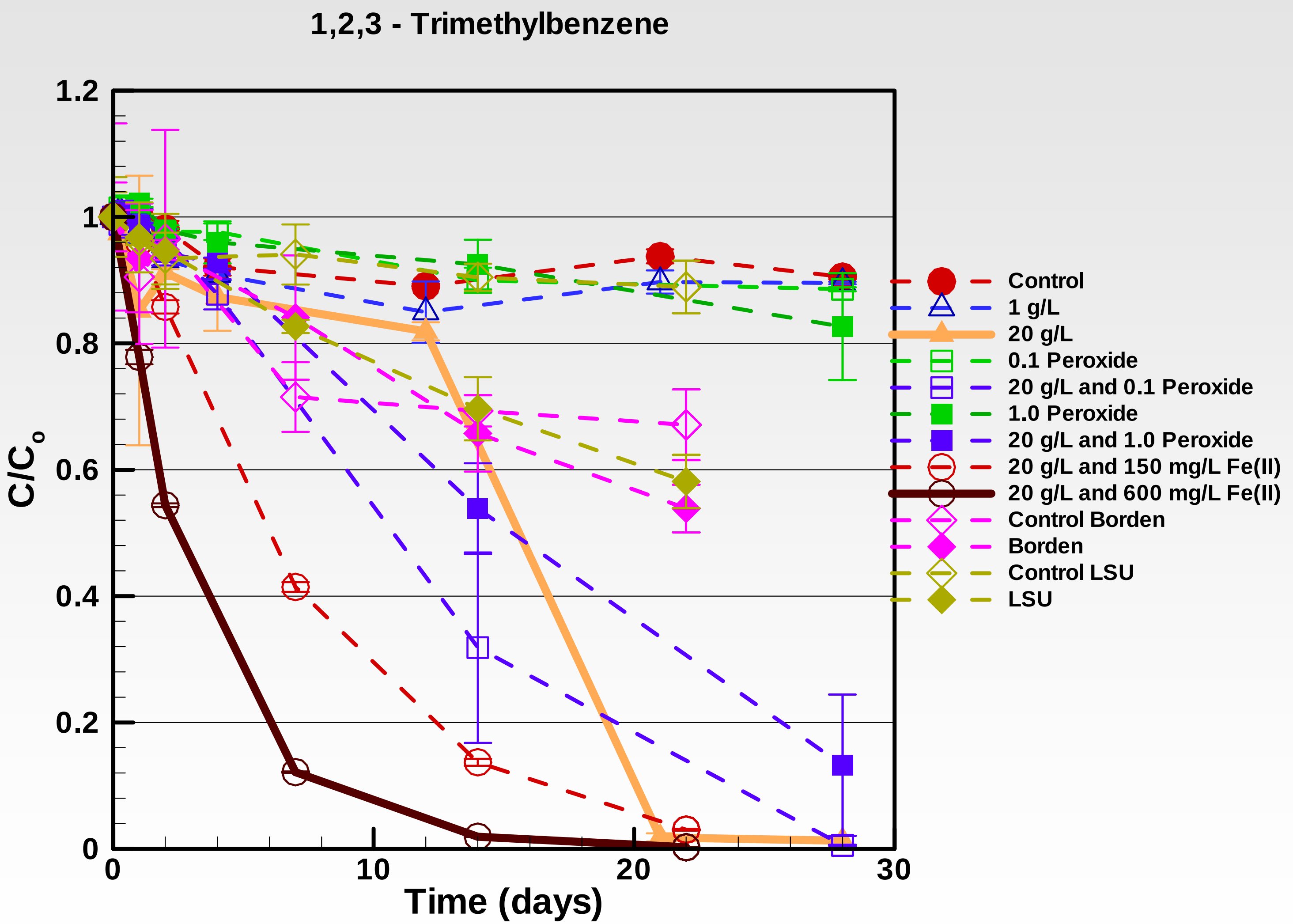
Xylenes Results



TMB Results


1,2,3 - Trimethylbenzene
C/C$_o$
Time (days)
0
0.2
0.4
0.6
0.8
1
1.2
0
10
20
30
Control
1 g/L
20 g/L
0.1 Peroxide
20 g/L and 0.1 Peroxide
1.0 Peroxide
20 g/L and 1.0 Peroxide
20 g/L and 150 mg/L Fe(II)
20 g/L and 600 mg/L Fe(II)
Control Borden
Borden
Control LSU
LSU

TMB Results



1,2,3 - Trimethylbenzene
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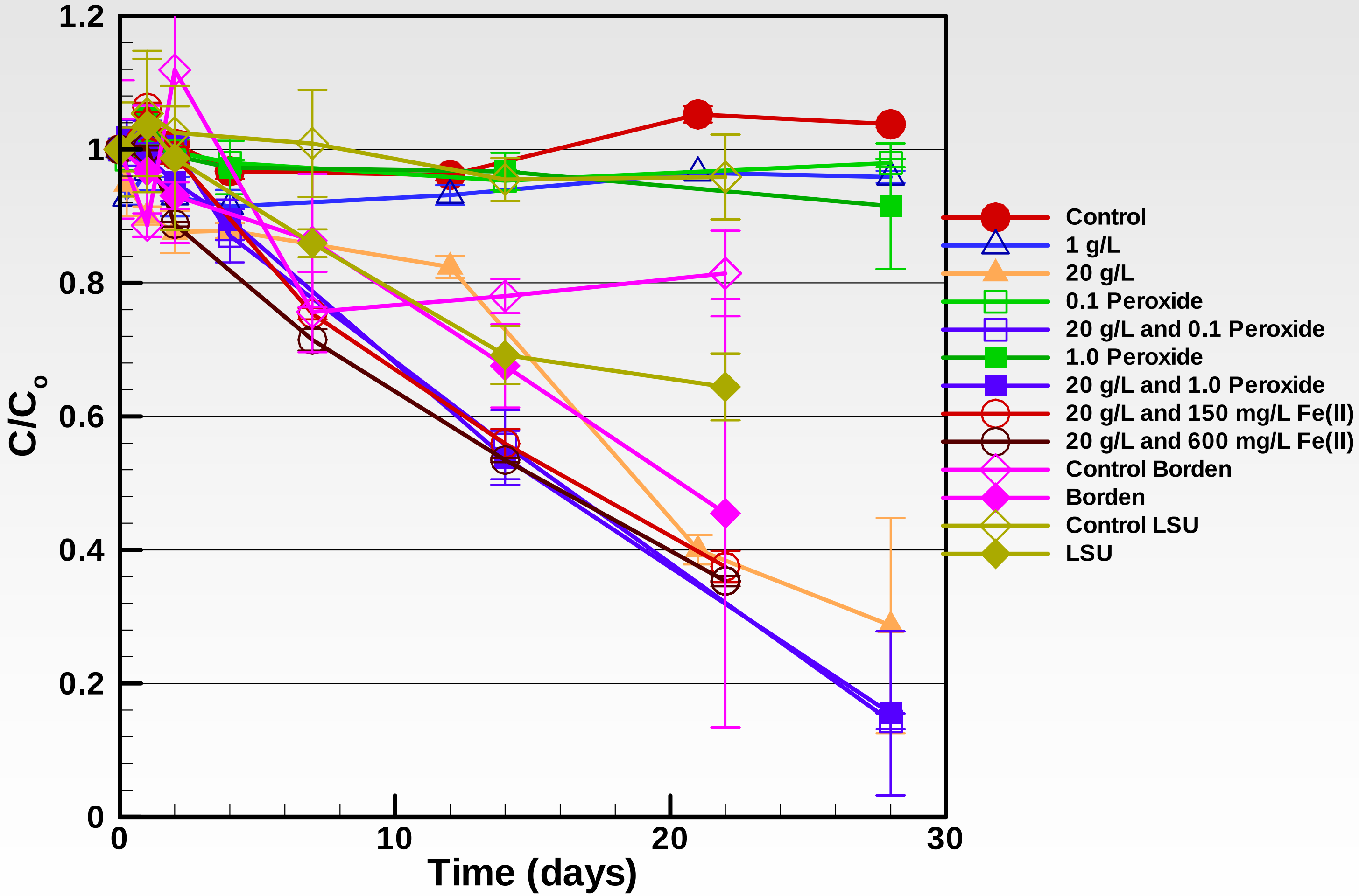
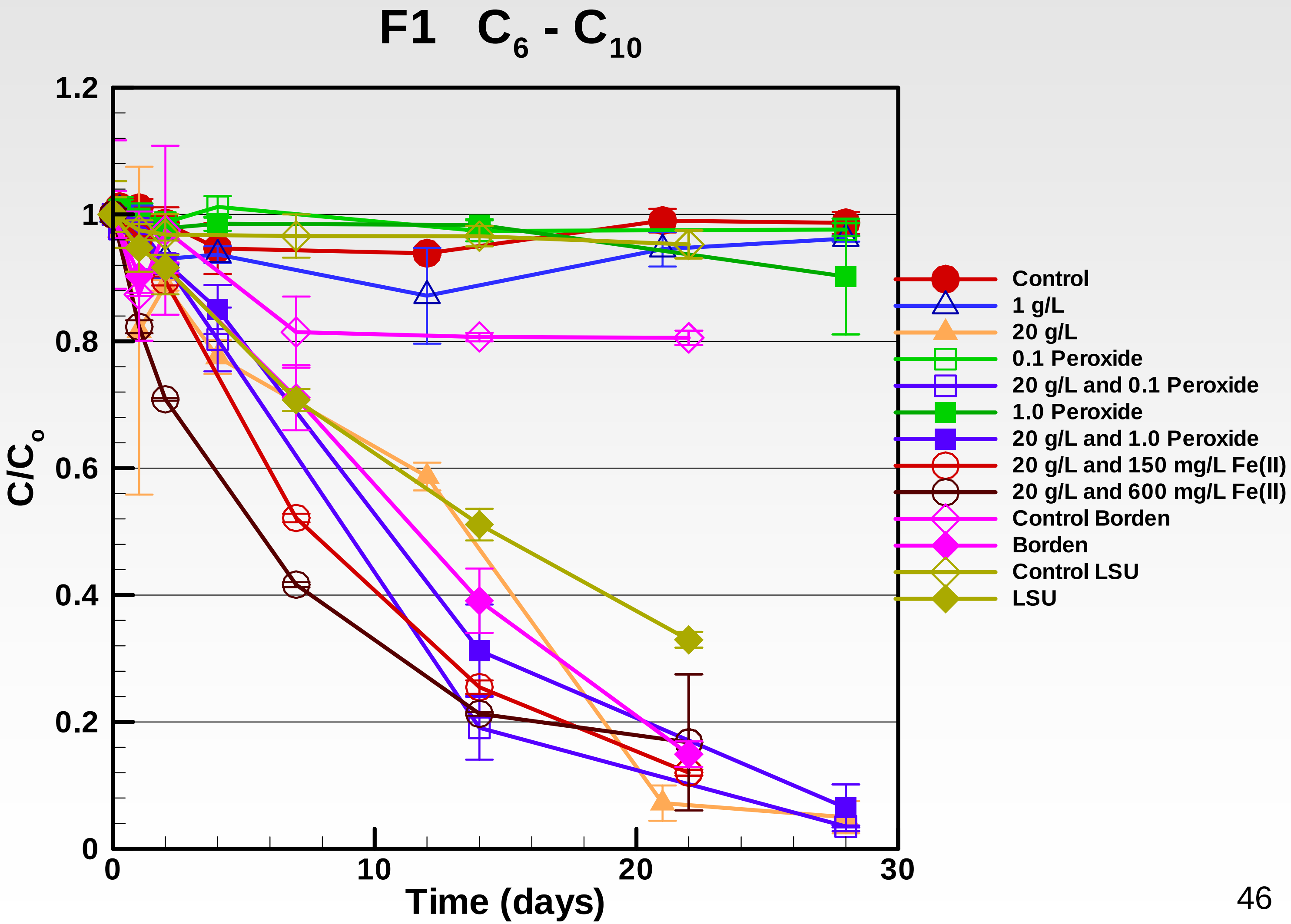
20 g/L and 150 mg/L Fe(II)
20 g/L and 600 mg/L Fe(II)
Control Borden
Borden
Control LSU
LSU

Naphthalene Results



Bulk Petroleum Hydrocarbon Fractions Results



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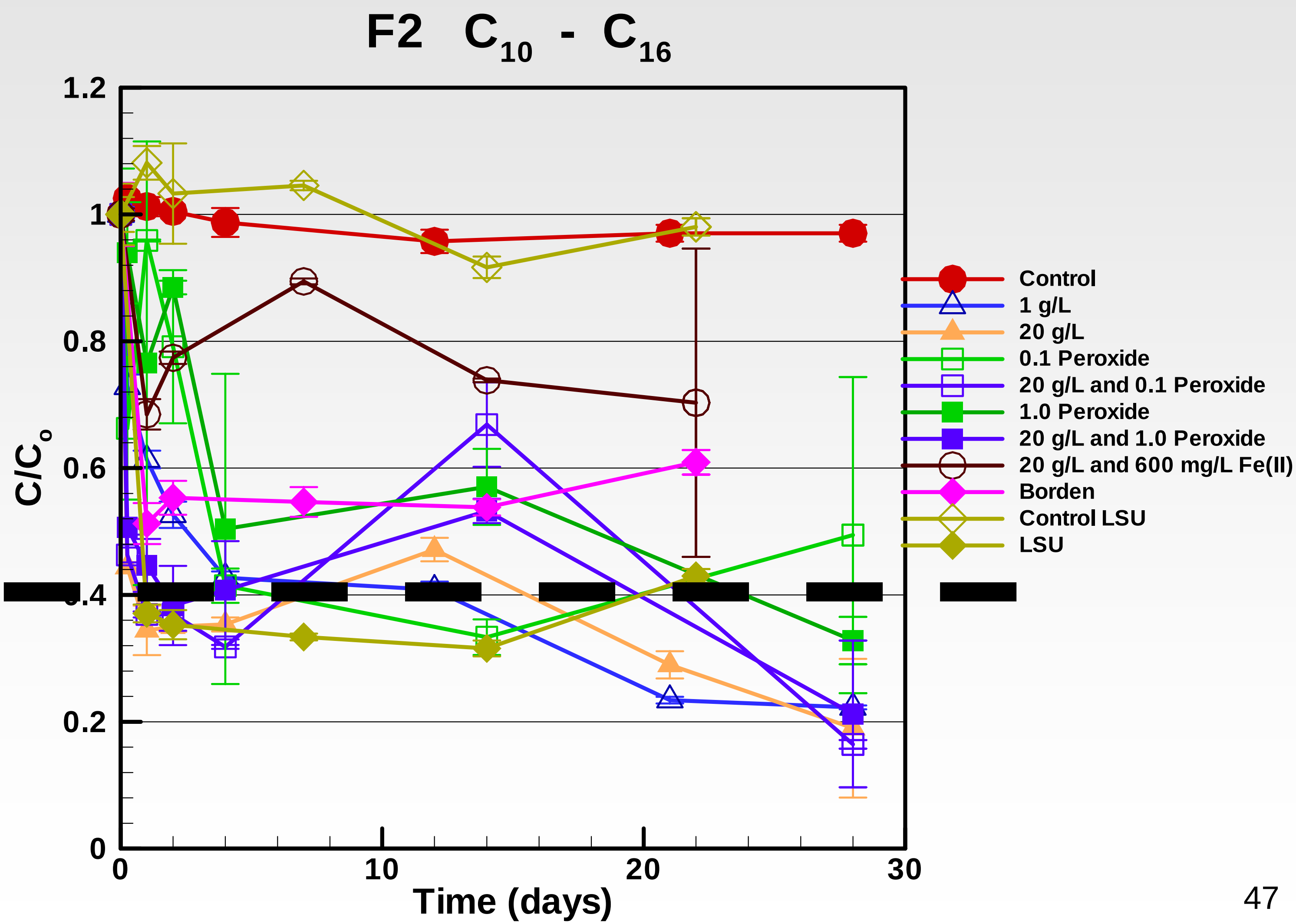

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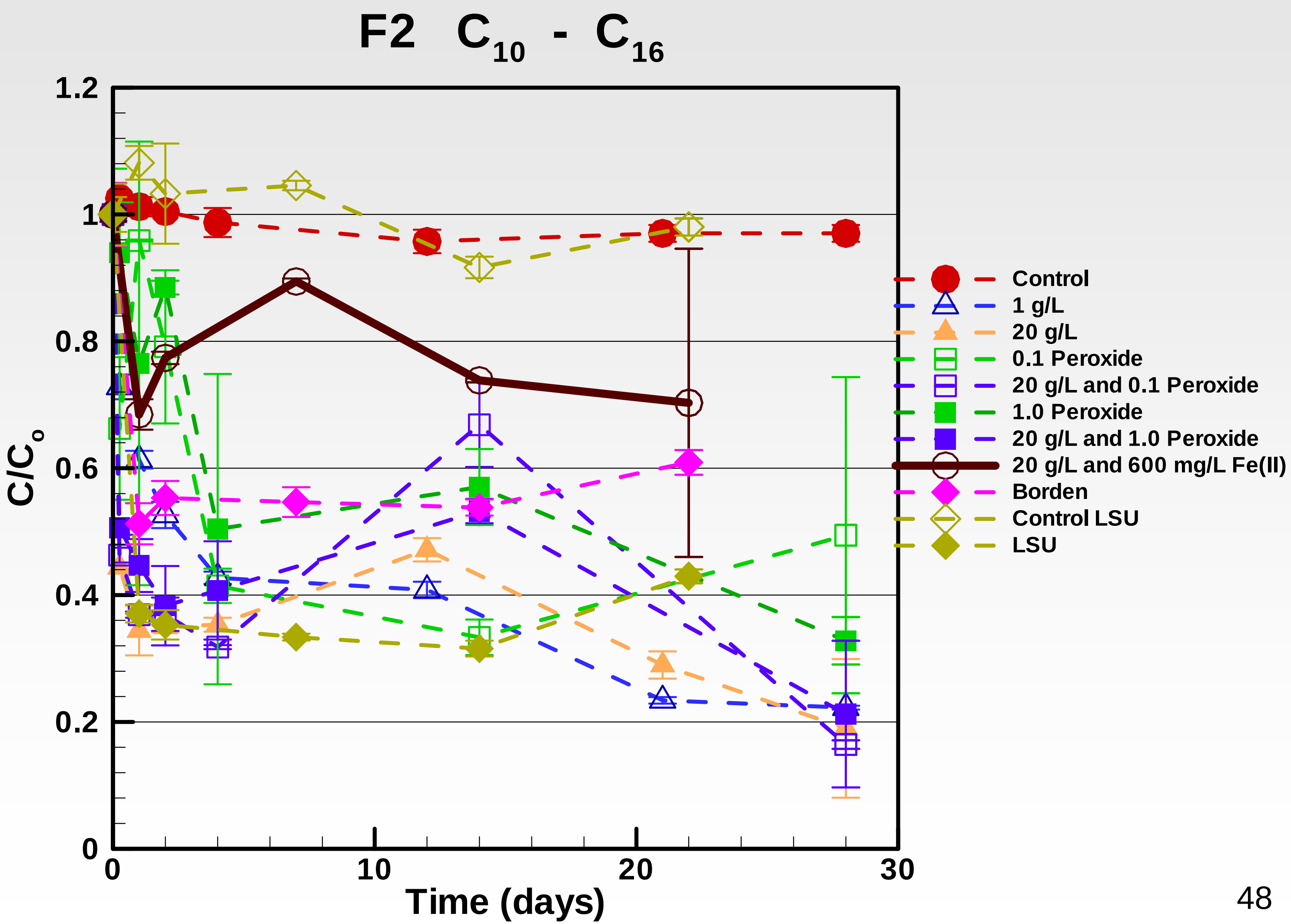
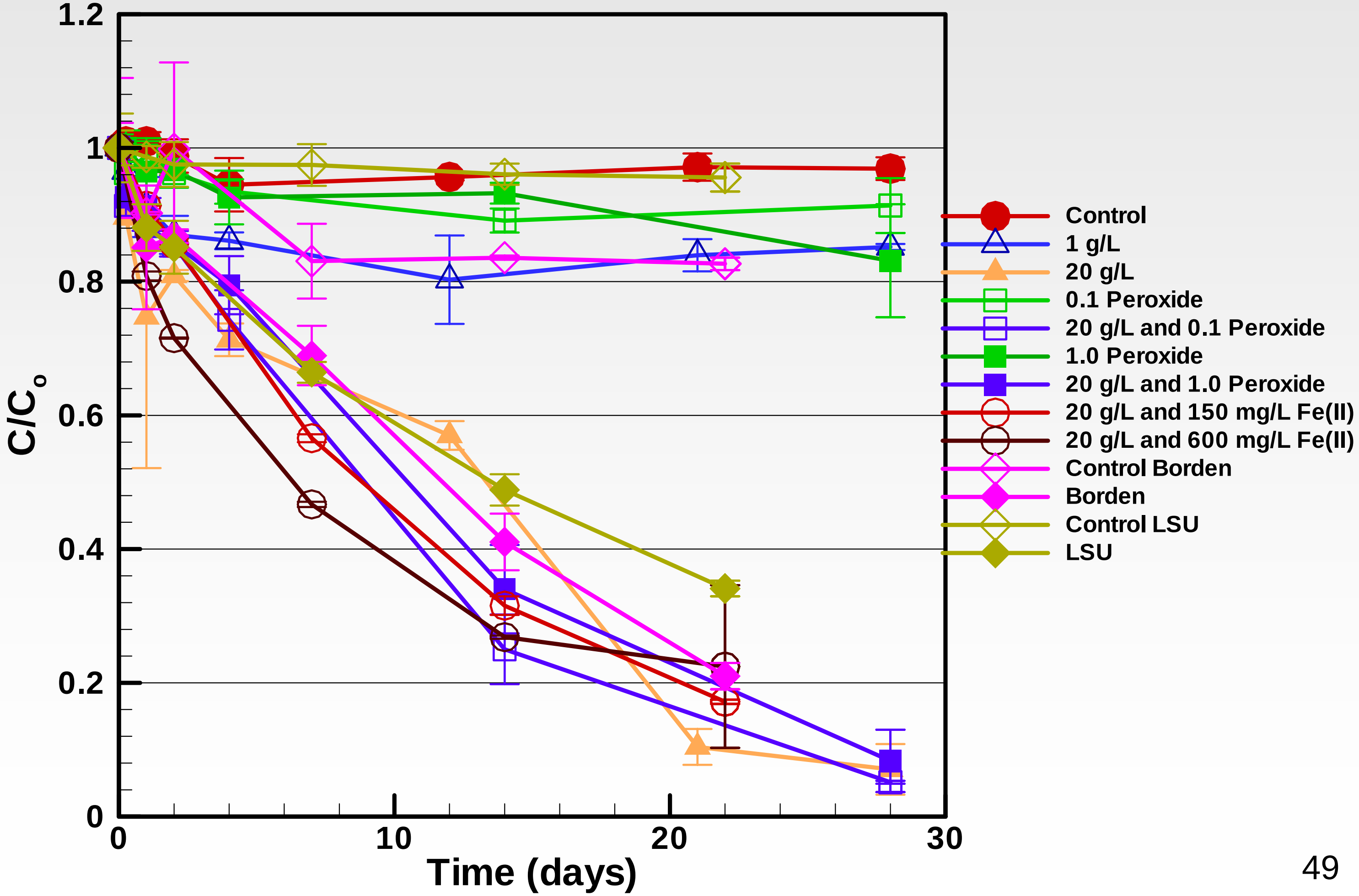


Total Petroleum Hydrocarbons (TPH) Results



Conclusions

- Persulfate appears to follow first order degradation in presence of aquifer materials
  - More stable at higher concentration

- Rate constants are highly correlated with reductive properties (COD, Fe-Amor, TOC)

Conclusions

- Unactivated persulfate at high concentration (~20 g/L) is capable of oxidizing gasoline compounds
- Activation of persulfate by peroxide and chelated ferrous iron enhances the oxidation rates in general

Conclusions

- Chelated ferrous produced the best results for BTEX, TMBs and F1 oxidation
  - F2 treatment was not effective
- Optimal molar ratio of peroxide to persulfate may be required for maximizing oxidation of gasoline

Conclusions

- F1 fraction was readily oxidizable
- F2 fraction stalled after nearly 60% oxidation

Acknowledgements

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Thanks