Destruction of TCE Using Oxidative and Reductive Pathways as Potential In-Situ Treatments for Contaminated Paducah Groundwater

PI: Dibakar Bhattacharyya*

Post Doc: D. Meyer
Ph.D. Students: S. Lewis, Y. Li, J. Xu, Y. Tee

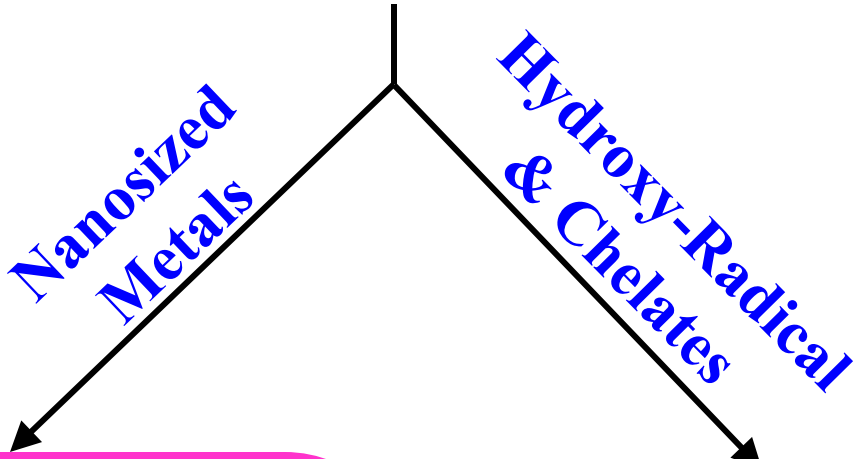
UK Dept. of Chemical & Materials Engineering

Quarterly KRCEE DOE Meeting

February 2, 2007

*Email: db@engr.uky.edu
Phone: 859-257-2794

Removal of TCE at Ambient Temperature



Reductive Dechlorination of TCE

$(nano)Fe^0 + TCE \rightarrow Fe^{2+} + Ethane + 3Cl^-$

$(Bulk)Fe^0 + TCE \rightarrow Fe^{2+} + intermediates + nCl^-$

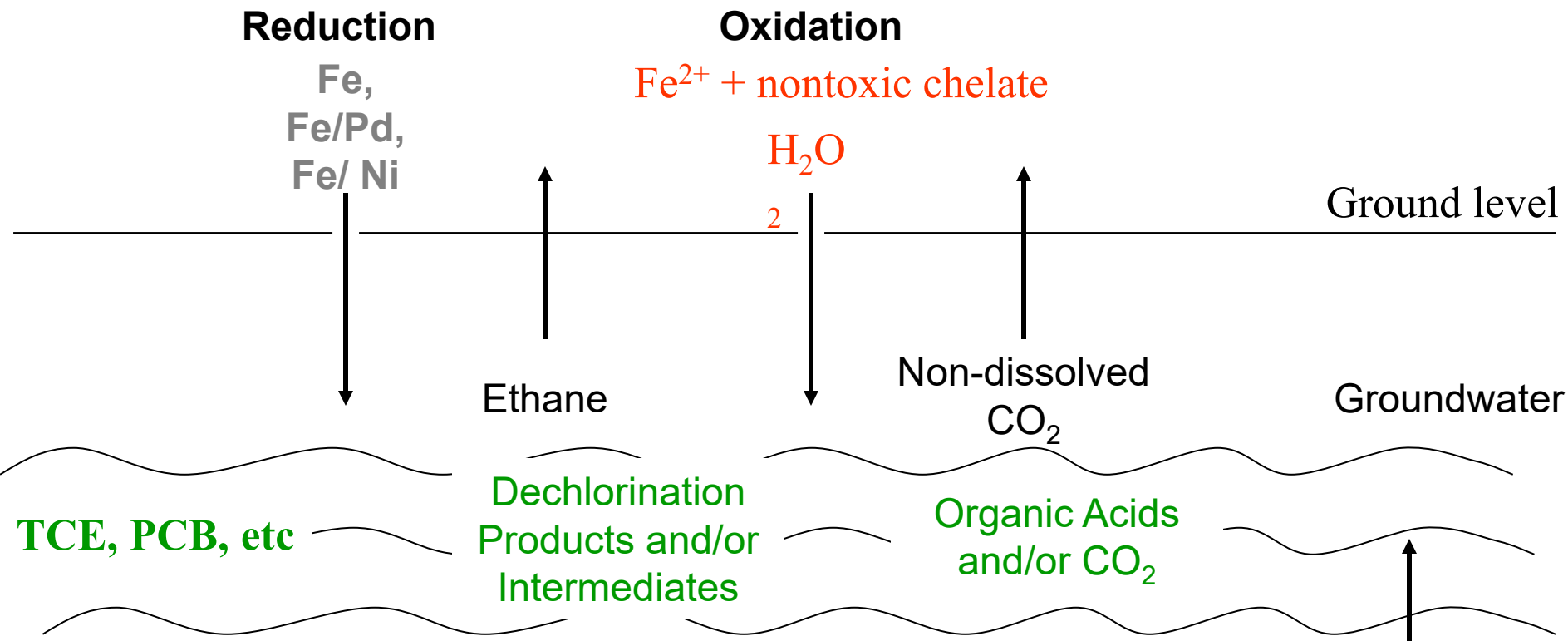
Systems Used:
Zerovalent metals (**Fe**), Bimetallic systems (**Fe/Pd, Fe/Ni**), Supported Platforms

Oxidative Destruction of TCE

$TCE + OH^{\cdot} \rightarrow CO_2$, Organic Acids

Systems Used:
Standard Fenton Reaction, Modified Fenton Reaction using **nontoxic chelate (citrate, gluconic acid) (L)** as a chelating agent (**FeL**).

Groundwater Remediation Using Combined Strategies For Reduction and Oxidation



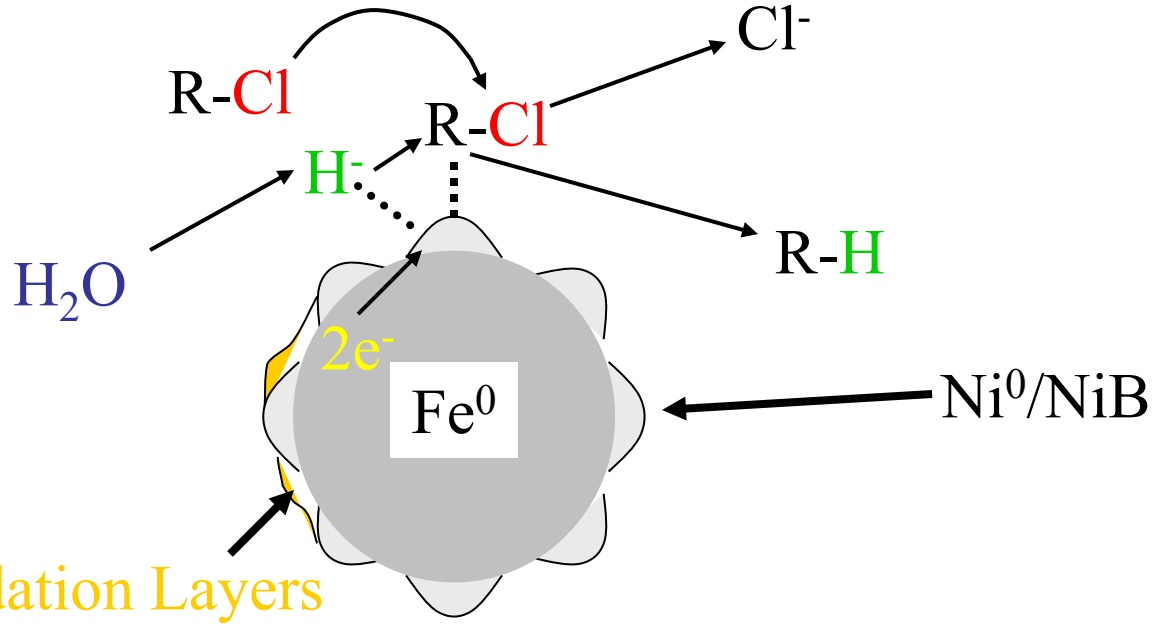
Enhanced downstream bio-attenuation of products because of biodegradable chelate (gluconic acid, citrate)

Reductive Dechlorination: Hydrogenolysis and Bimetallic Systems

- A catalyzed **Hydrogenolysis** mechanism is believed to exist for **bimetallic** ZVM systems.

Ni-Promoted Hydrogenolysis

Adapted from
Mallouk, et. al., (2002)

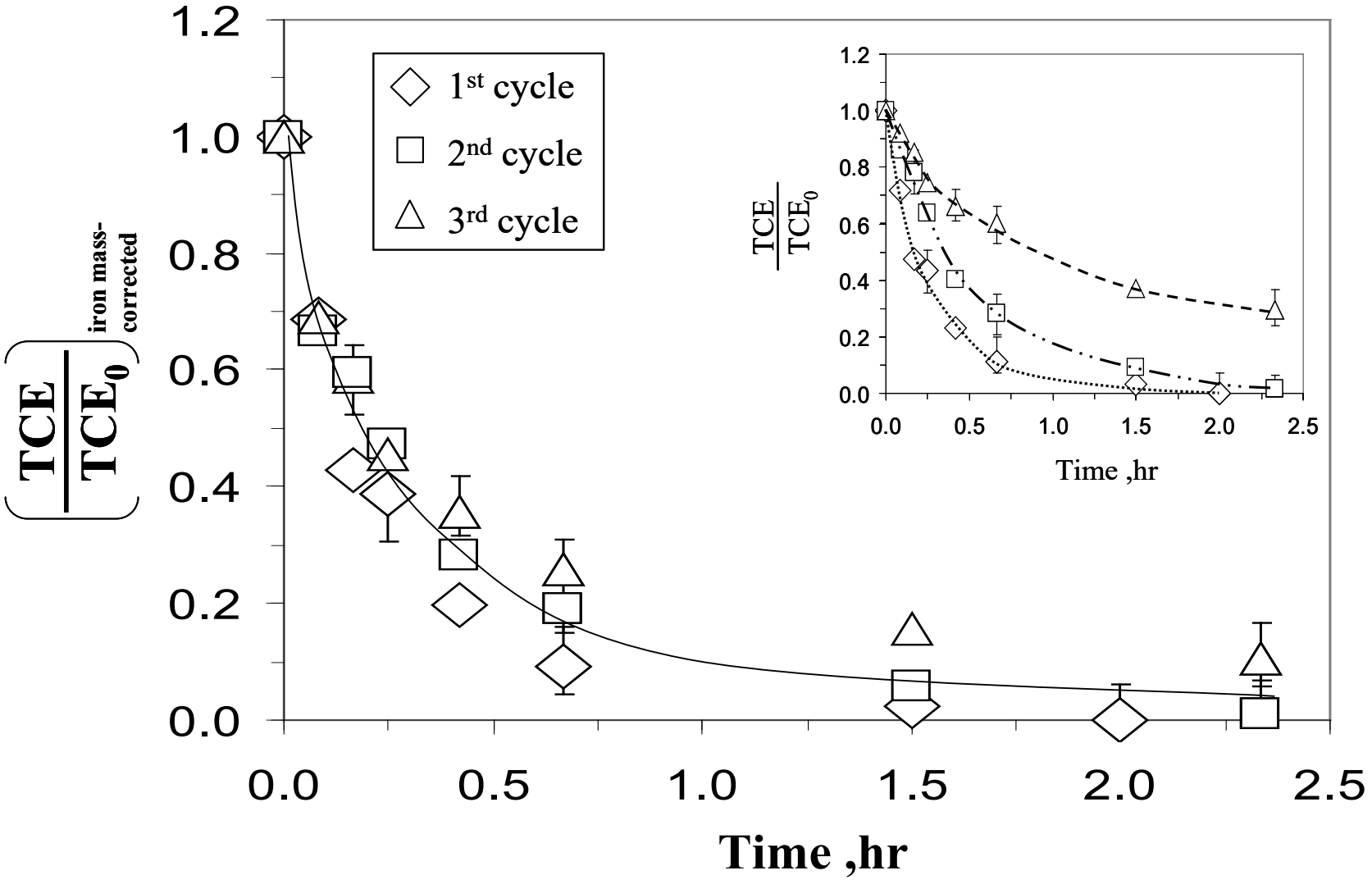


- This mechanism is supported by the fact that dechlorination rates increase as the H-promoting ability of the 2nd metal increases:

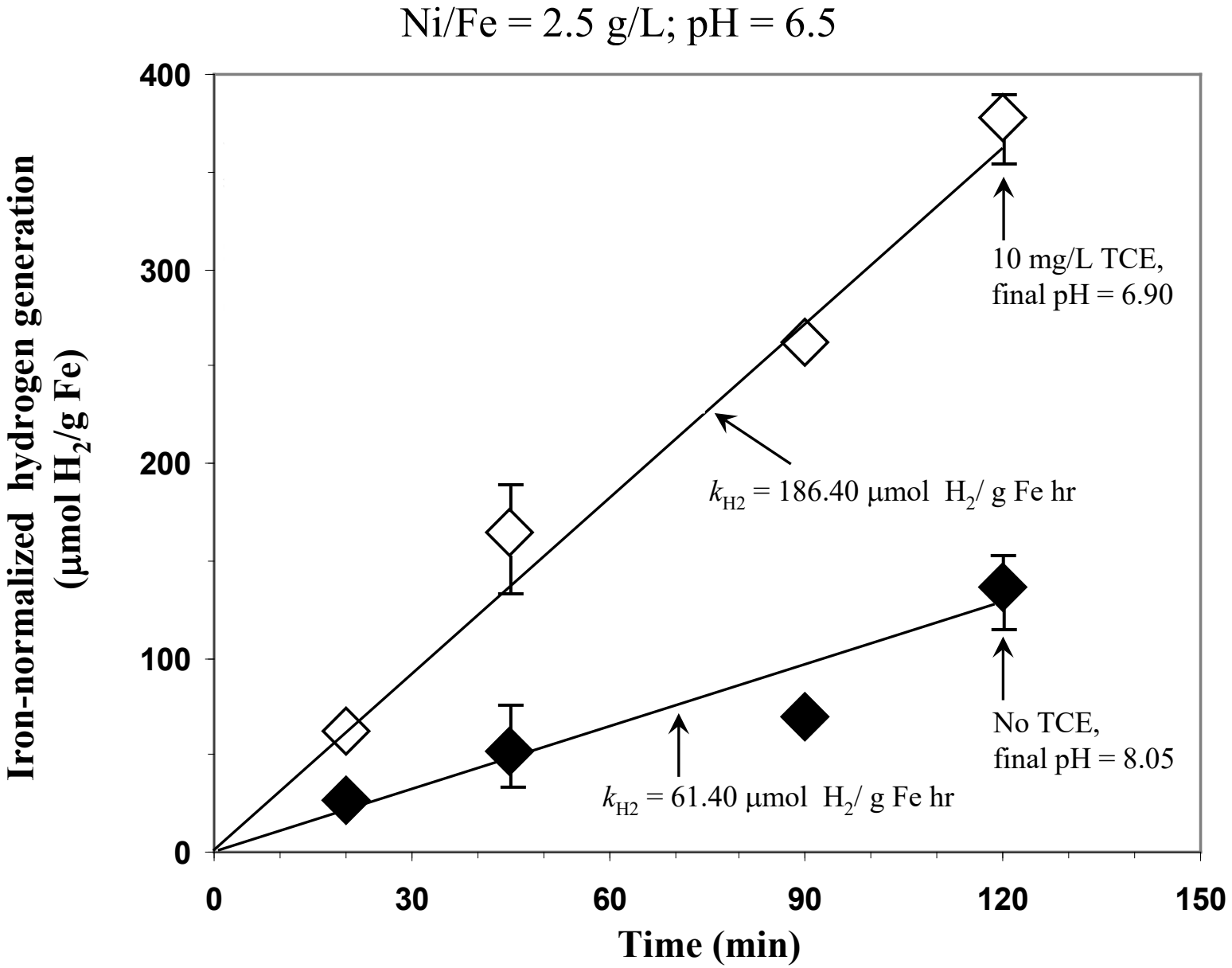
$$k_{Pt/Fe} > k_{Pd/Fe} > k_{Ni/Fe} > k_{Fe}$$

Batch Cycle Study for TCE Degradation by Ni/Fe (Ni = 20 wt%) Nanoparticles in Deoxygenated Water with Headspace:

Metal Loading = 2.5 g/L; pH = 6.5 ; TCE_0 = 10 mg/L



Total H_2 produced as a Function of Time for Ni/Fe (Ni = 20 wt%) Nanoparticles Both With and Without TCE Degradation:

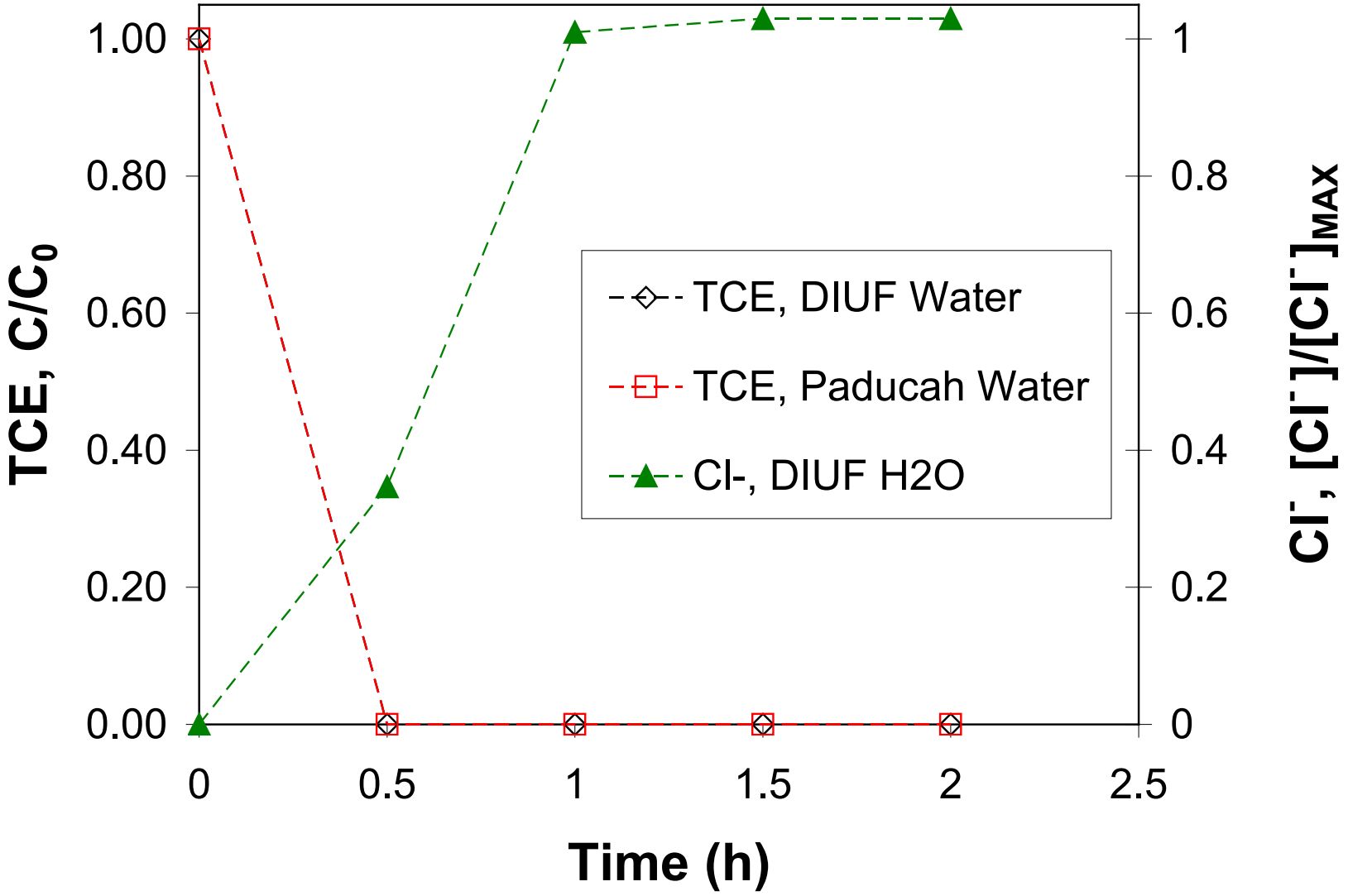


Aspects to Address for Successful TCE Dechlorination Using Direct Injection of Bimetallic Nanoparticle Systems

- What **composition** and **metal loading** are necessary for rapid and efficient TCE dechlorination? (**batch** data)
- Will the **presence of other chemical species** present in **Paducah groundwater and soil** alter the performance of Fe-based nanoparticle dechlorination systems? (**batch** and column experimental data)
- What impact, if any, will **dissolved oxygen** have on dechlorination kinetics? (**batch** data)
- What type of **mobility** will **nanoparticles** have while moving within plumes? (theoretical modeling)

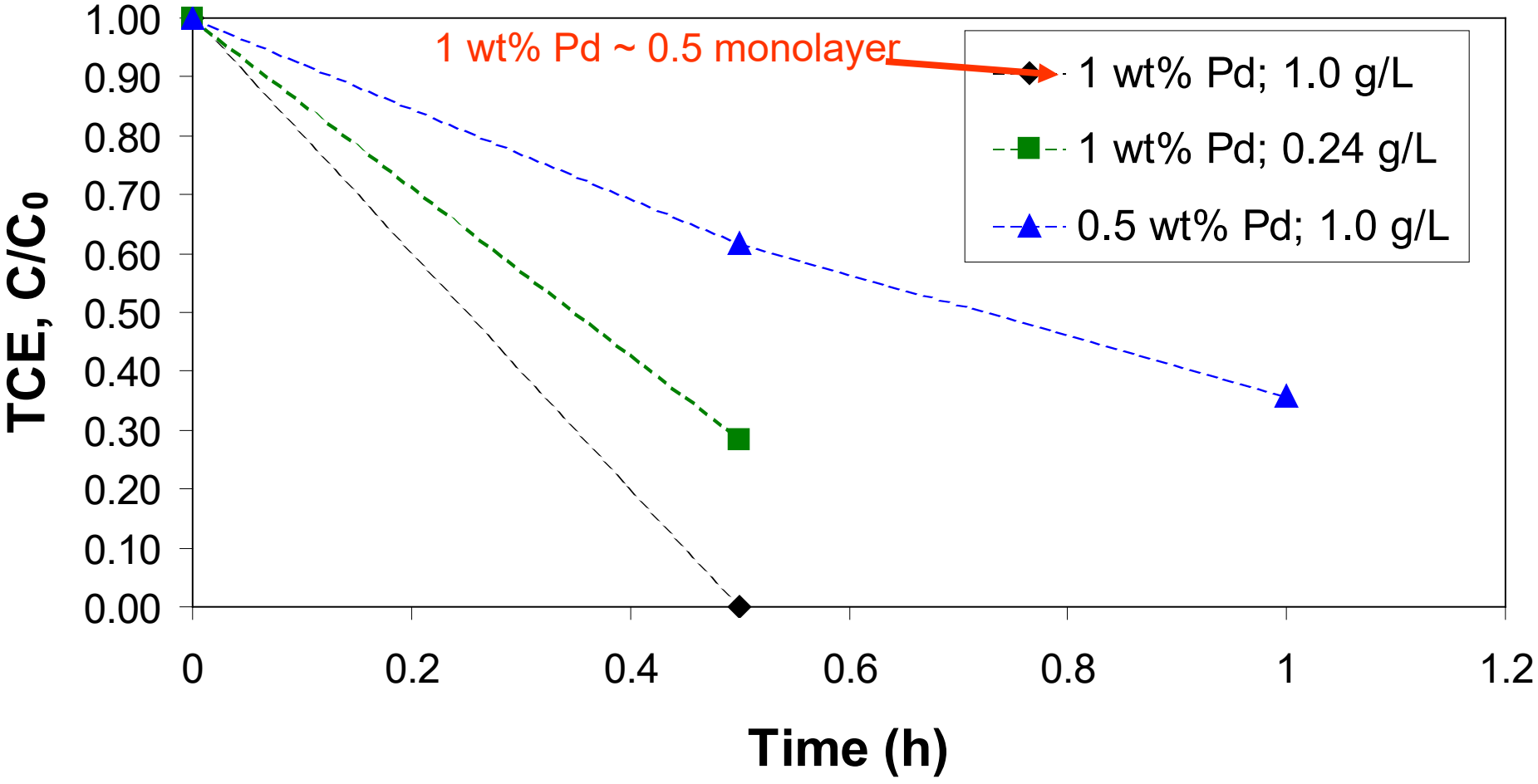
Dechlorination of TCE Using Fe/Pd Nanoparticles (1 wt% Pd) In Deoxygenated Water with Headspace:

Metal Loading = 1.0 g/L; pH = 6; C_0 = 16.6 mg/L TCE



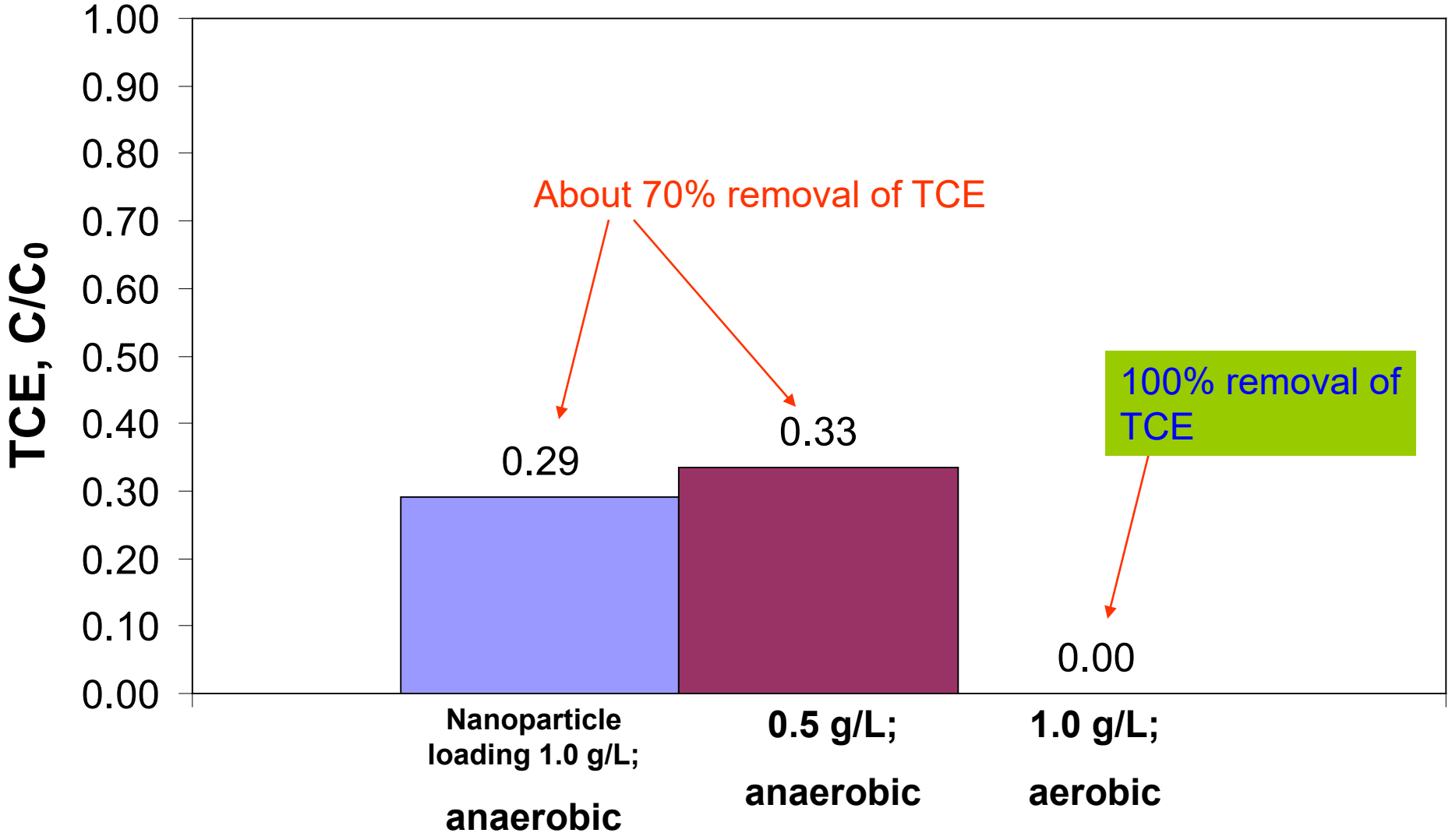
Dechlorination of TCE in Deoxygenated Paducah Water Using Fe/Pd Nanoparticles with Variable Metal Conditions:

C_0 = 20.5 mg/L; pH = 5



Dechlorination of TCE Using Fe/Pd Nanoparticles (1 wt% Pd) In Paducah Water with Gravel:

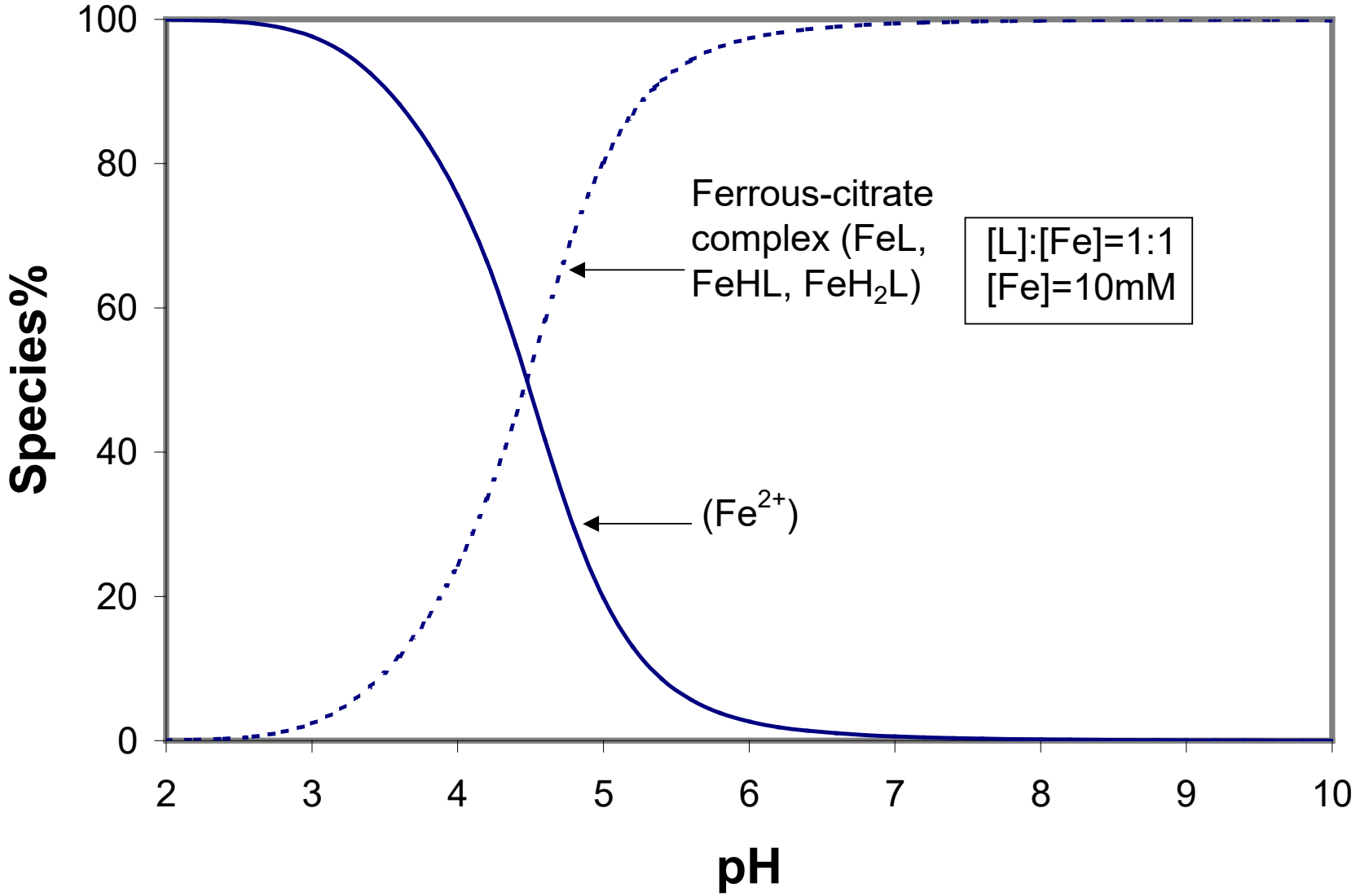
pH = 6; C_0 = 21.9 mg/L TCE, Reaction time = 0.5 hr



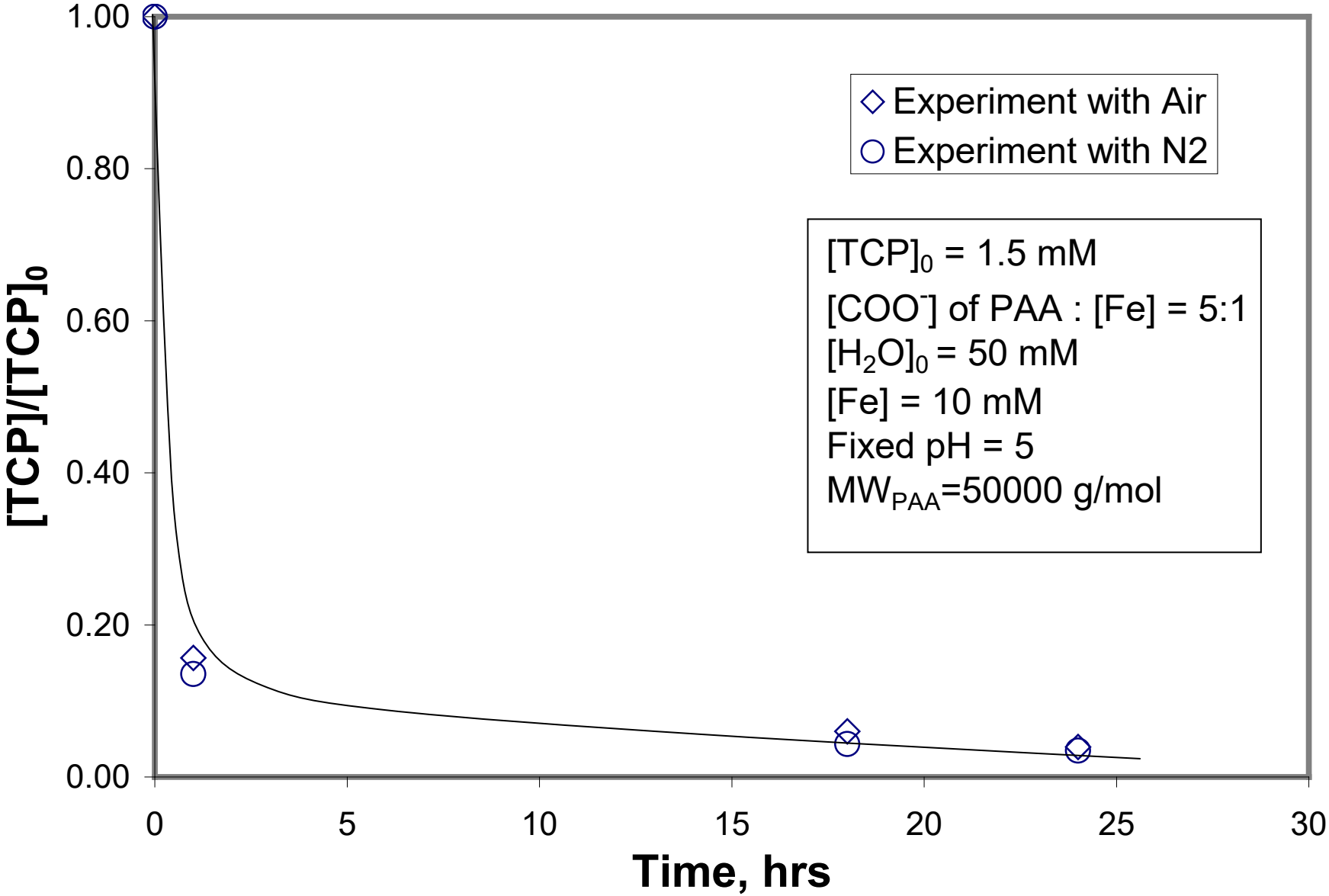
Why Chelate-Based Modified Fenton's Reaction?

- Controlled release of Fe^{2+}
- Prevent Fe(II) oxidation
- At near neutral pH, prevent $Fe(OH)_3$ precipitate by complexing with Fe(III)
- Have a better H_2O_2 utilization during the reaction
- Hydroxy radical and superoxide radical formation near neutral pH operation
- Potential biodegradation enhancement
- Chelate can also be immobilized in nano-particles

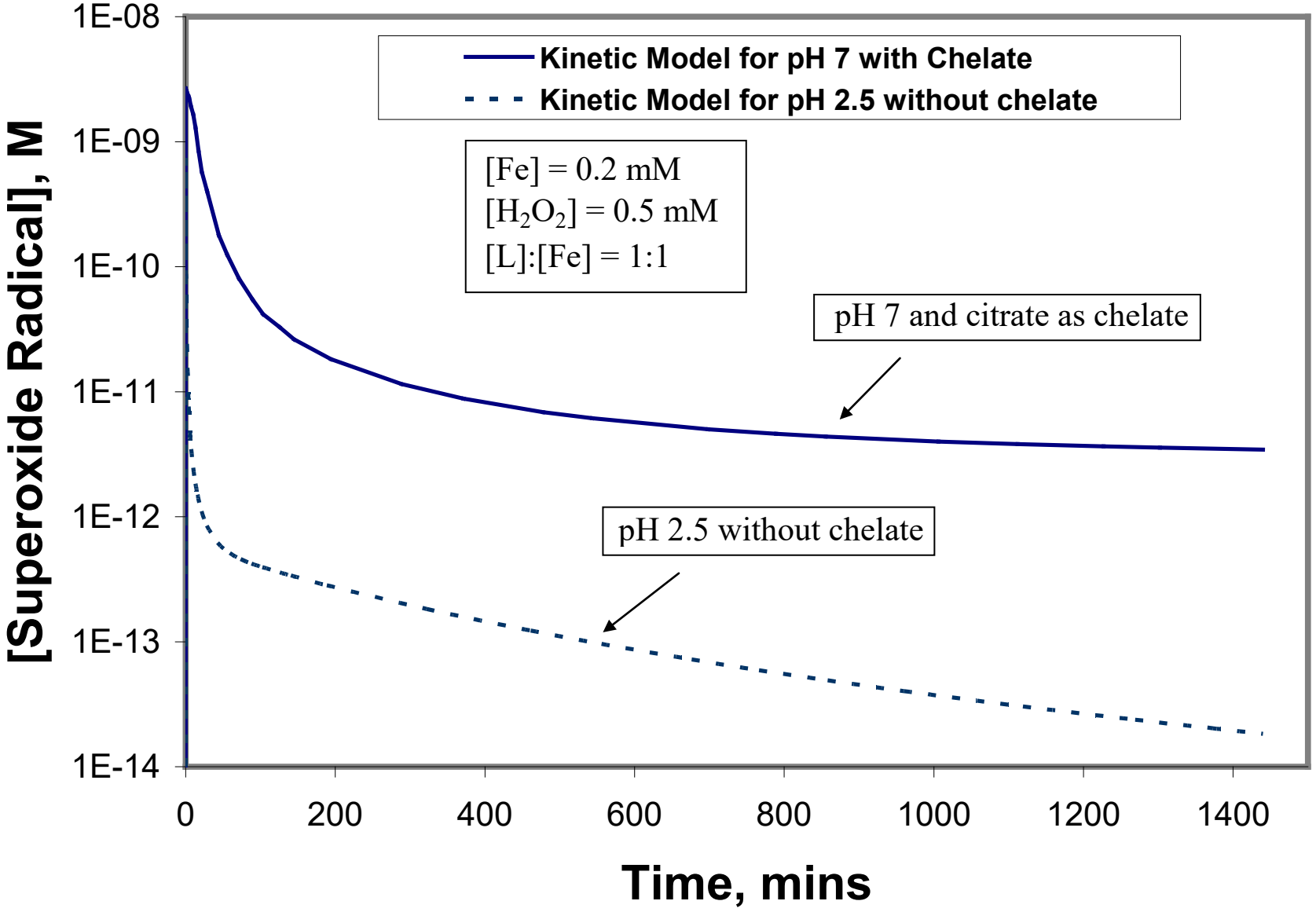
Iron-Citrate Species Distribution



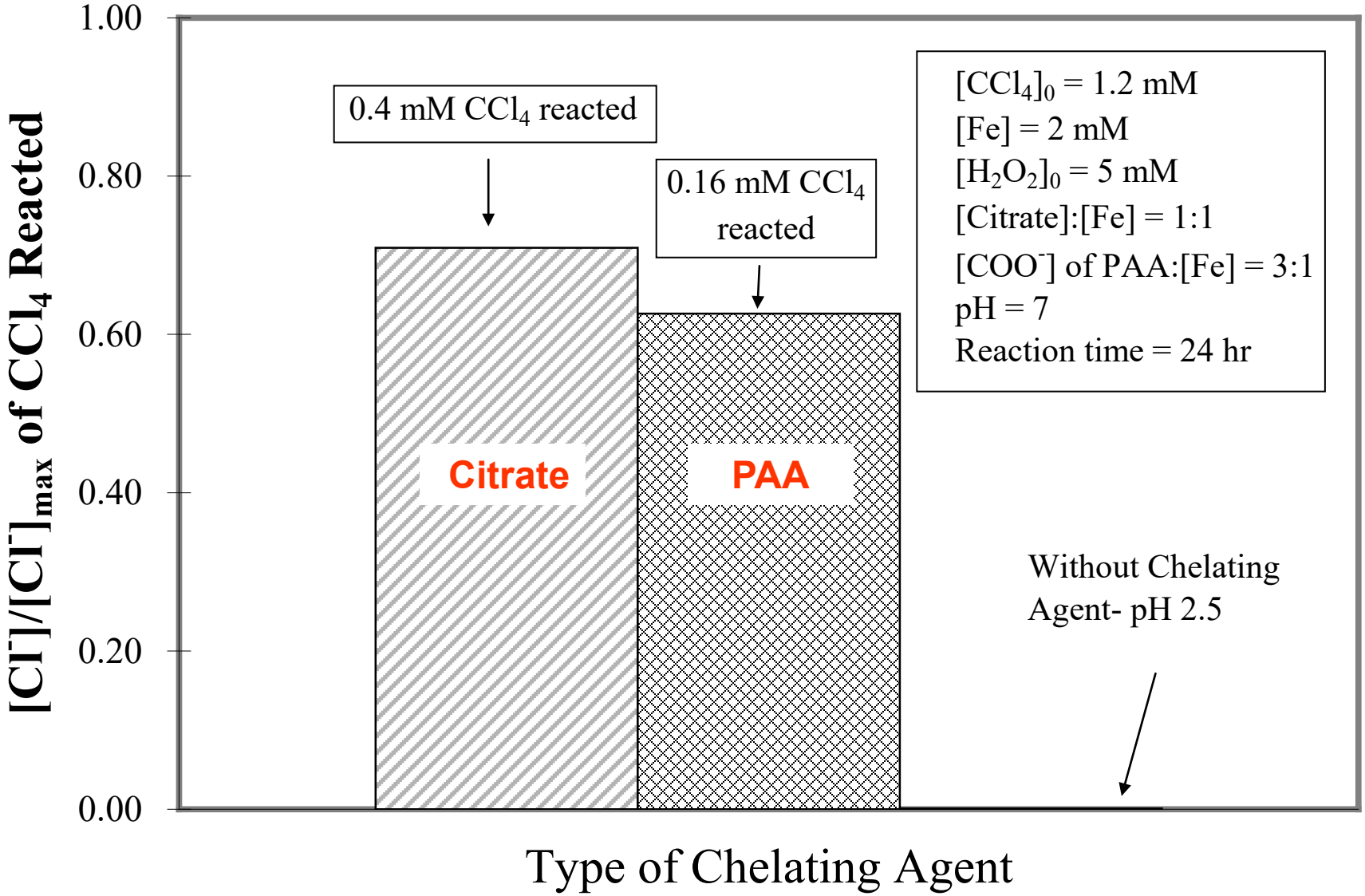
Effect of Dissolved Oxygen for TCP Oxidation by Fe^{2+} + PAA + H_2O_2 System (chelate modified system)



The Predicted Profiles of superoxide [$O_2^{\bullet -}$] for the Standard and Modified Fenton Reactions



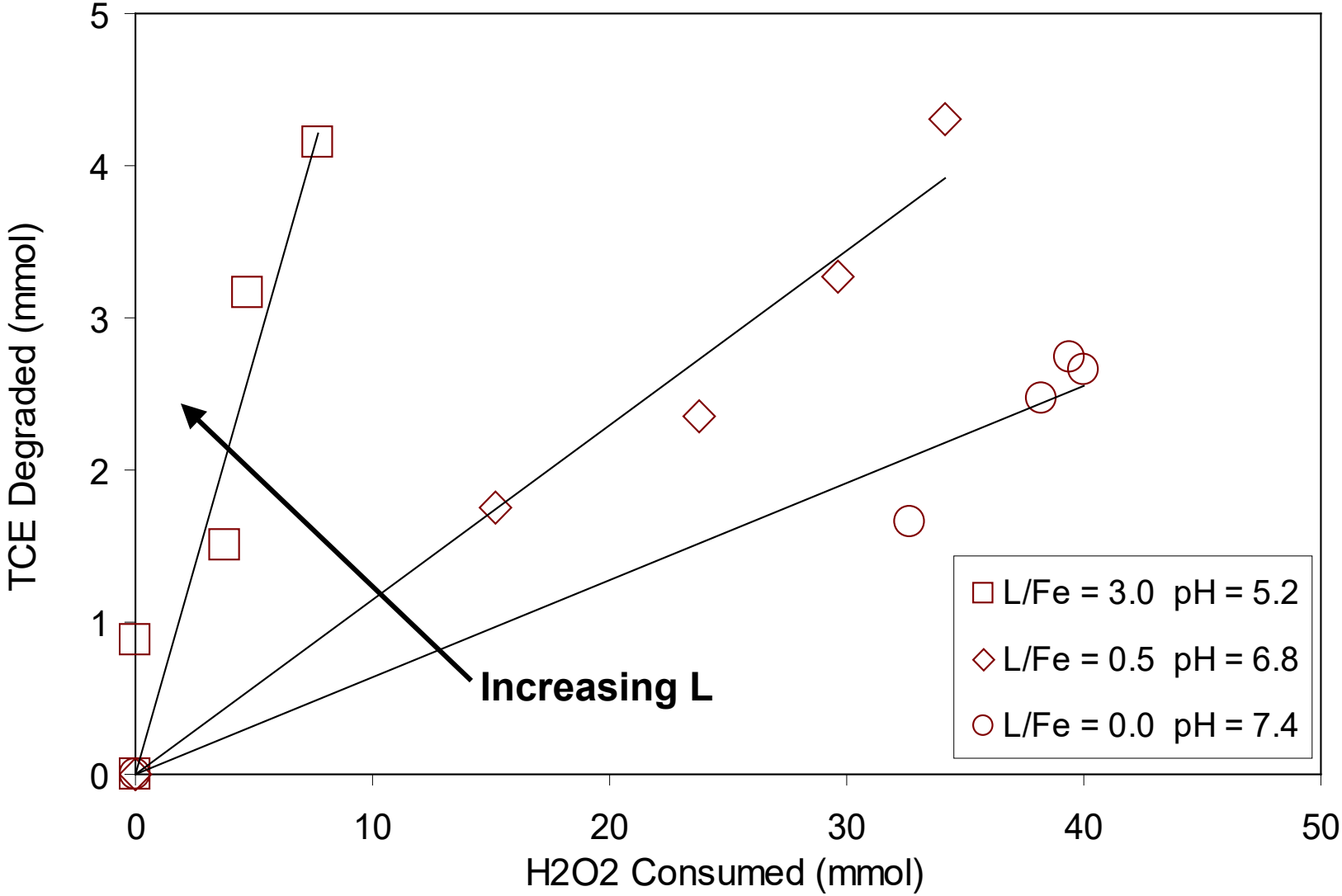
Chloride Formation During CCl_4 dechlorination under Standard and Chelate Based Modified Fenton Reaction at 24 hr Reaction Time



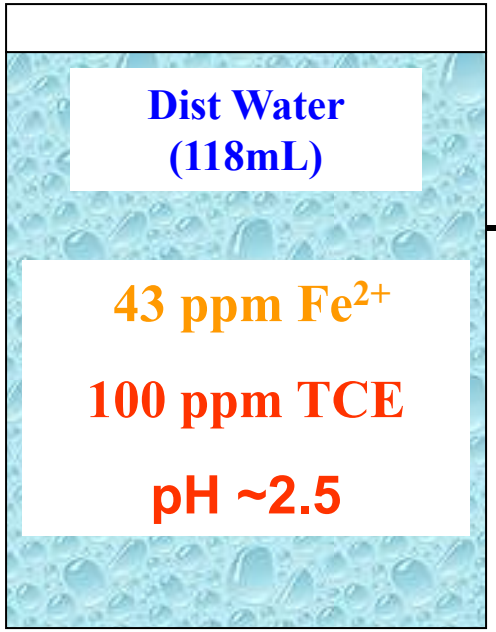
Topics to Address for Successful Dechlorination Using Chelate-Based Modified Fenton's Reaction

- What **reactant ratios ([Fe]:[H_2O_2]:[L])** and **total reactant doses** are necessary for rapid and efficient dechlorination?
- Will the **presence of other chemical species** present in **Paducah groundwater and soil** alter the performance of dechlorination systems involving chelate-based modified Fenton's reaction?
- How can **material requirements** be **reduced** using on-site production of peroxide and chelate?

TCE Degradation as a Function of Peroxide Consumed for Varying Citrate (L)-to-Fe Ratios Showing the Potential Reduction in Peroxide Needs for Chelate-Based Systems



Standard Fenton Reaction (pH=2.5) Using Paducah Water With Varying Fe(II):H_2O_2 Ratio



100-mL Vial
(120-mL volume)

Add H_2O_2

Molar Ratios of
TCE:Fe:Citrate:H_2O_2
1:1:4
1:1:8

Reaction
Continuous pH
Adjustment (pH~2.5)

Control Run
%TCE Remaining
87.5%

GC/MS Analysis

TCE:Fe:Citrate:H_2O_2	%TCE Reacted at 10 hr
1:1:4	90%
1:1:8	100%

Distilled Water

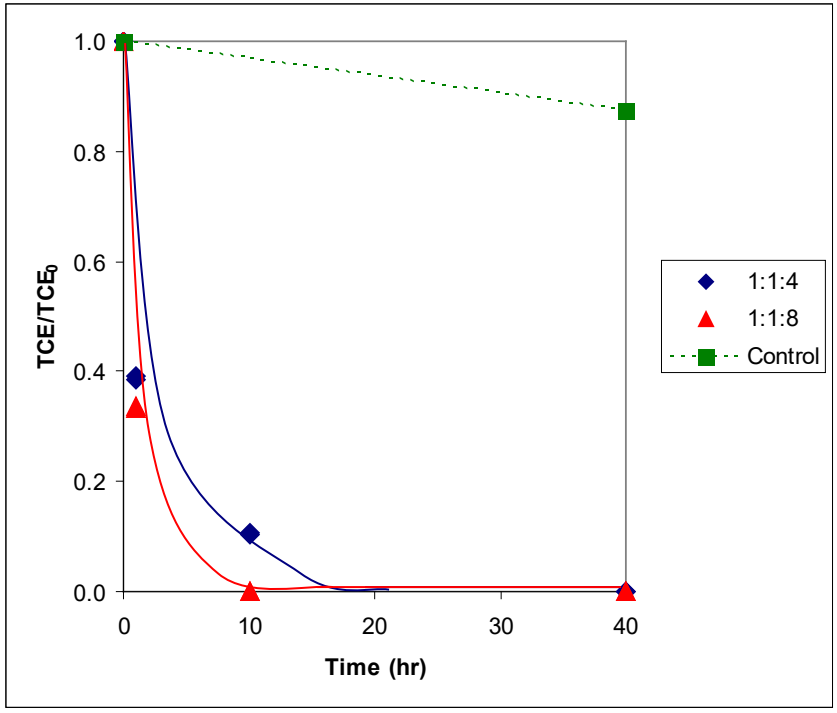
TCE:Fe:Citrate:H_2O_2	%TCE Reacted at 10 hr
1:1:4	100%
1:1:8	100%

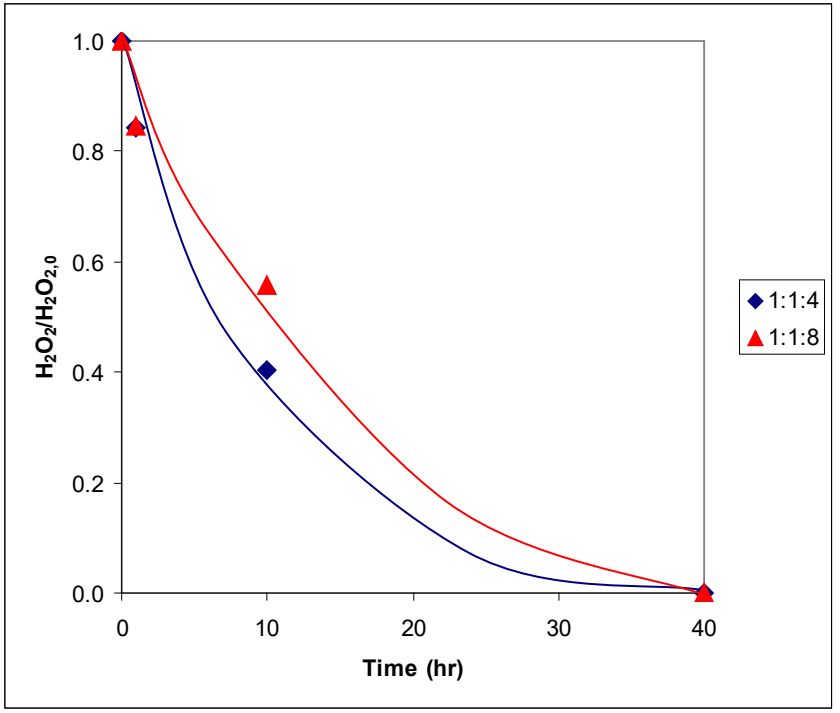
Standard Fenton Reaction (pH=2.5) Using Paducah Water With Varying Fe(II):H_2O_2 Ratio

TCE and H_2O_2 concentrations as a function of Time for TCE:Fe:Citrate:H_2O_2 molar ratios of 1:1:4 and 1:1:8. Initial TCE concentration of 100ppm.

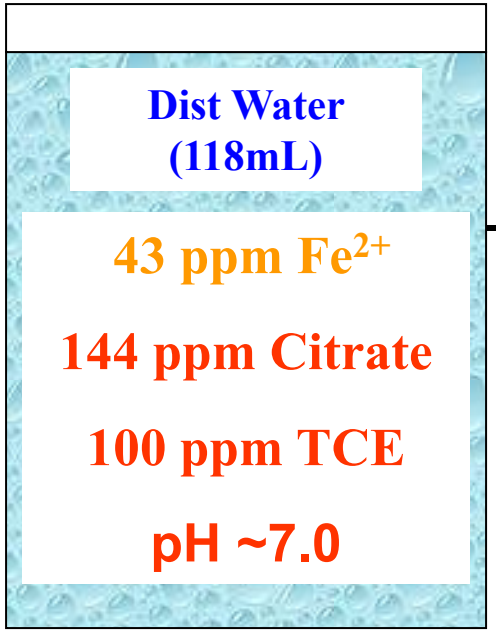
Control: TCE, Citrate, Fe (no H_2O_2)

Note: Data represents individual runs sampled at indicated time





Modified Fenton Reaction (pH=7.0) Using Paducah Water With Varying Fe(II):H_2O_2 Ratio



100-mL Vial
(120-mL volume)

Add H_2O_2

Molar Ratios of
TCE:Fe:Citrate:H_2O_2
1:1:1:4
1:1:1:8

Reaction
Continuous pH
Adjustment (pH~7)

Control Run
%TCE Remaining
87.5%

Paducah Water

TCE:Fe:Citrate:H_2O_2	%TCE Reacted at 40 hr
1:1:1:4	52%
1:1:1:8	87%

Distilled Water

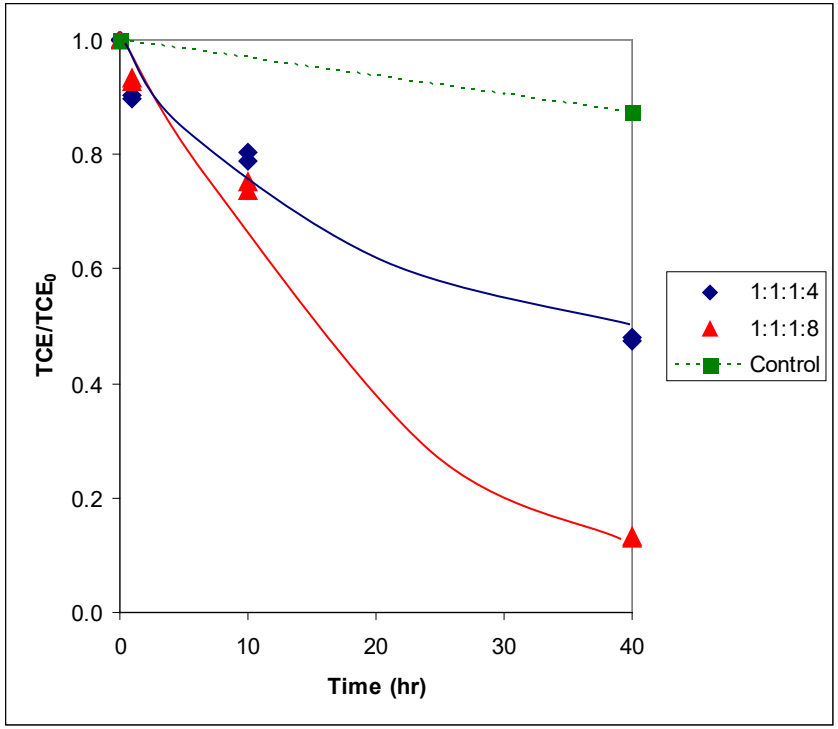
TCE:Fe:Citrate:H_2O_2	%TCE Reacted at 40 hr
1:1:1:4	~64%
1:1:1:8	~100%

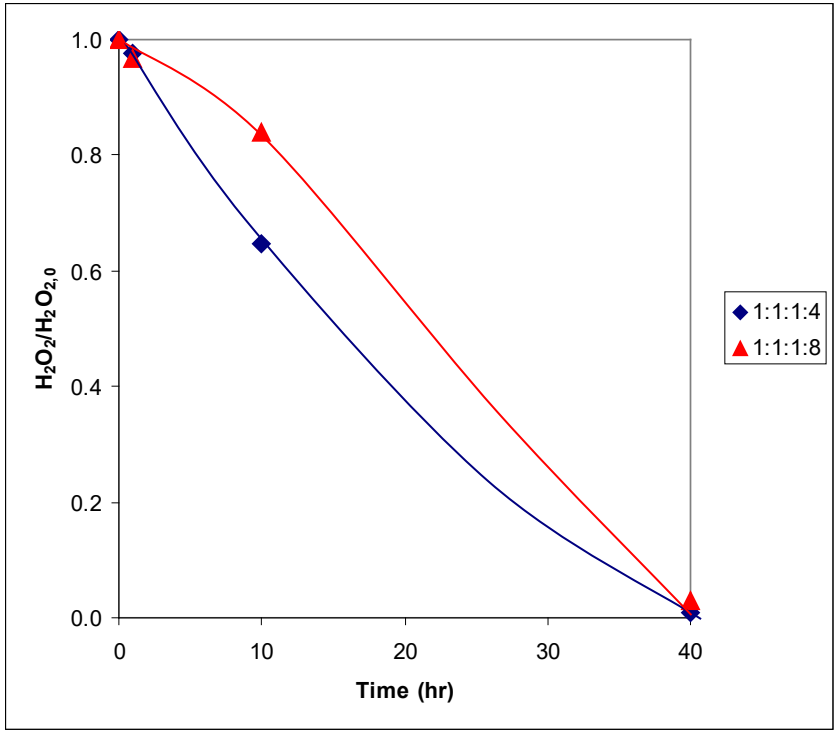
Modified Fenton Reaction (pH=7.0) Using Paducah Water With Varying Fe(II):H_2O_2 Ratio

TCE and H_2O_2 concentrations as a function of Time for TCE:Fe:Citrate:H_2O_2 molar ratios of 1:1:1:4 and 1:1:1:8. Initial TCE concentration of 100ppm.

Control: TCE, Citrate, Fe (no H_2O_2)

Note: Data represents individual runs sampled at indicated time





Summary of Accomplishments

- Chlorinated organic destruction in modified Fenton reaction is same for both aerobic and anaerobic conditions
- Water from the Paducah area produces lower TCE destruction rates than deionized water due to the presence of hydroxyl scavengers (near neutral pH operation); will need slightly higher H2O2
- The complete dechlorination of TCE using Fe/Pd (1 wt% Pd) can be achieved in under 30 minutes using a metal loading of 1 g/L (or less) and is not affected by the presence of background chemicals in Paducah water.
- Batch dechlorination results obtained in the presence of Paducah gravel showed >70 % TCE removal in 1 h for 21.0 mg/L TCE using 0.5-1.0 g/L Fe/Pd (1 wt% Pd).
- Preliminary results for reductive dechlorination under aerobic conditions suggests that the presence of O_2 has miminal impact for the Pd-protected Fe nanoparticles.