

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

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Quarterly KRCEE DOE Meeting

February 2, 2007

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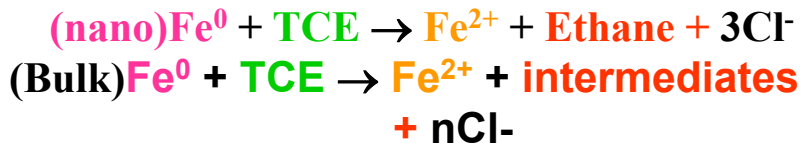
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Removal of TCE at Ambient Temperature

Nanosized Metals

Hydroxy-Radical & Chelates

Reductive Dechlorination of TCE



Systems Used:

Zerovalent metals (Fe), Bimetallic systems (Fe/Pd, Fe/Ni), Supported Platforms

Oxidative Destruction of TCE



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

Reduction

Fe,
Fe/Pd,
Fe/ Ni

Oxidation

$Fe^{2+} + \text{nontoxic chelate}$

H_2O

2

Ground level

Ethane

Non-dissolved
 CO_2

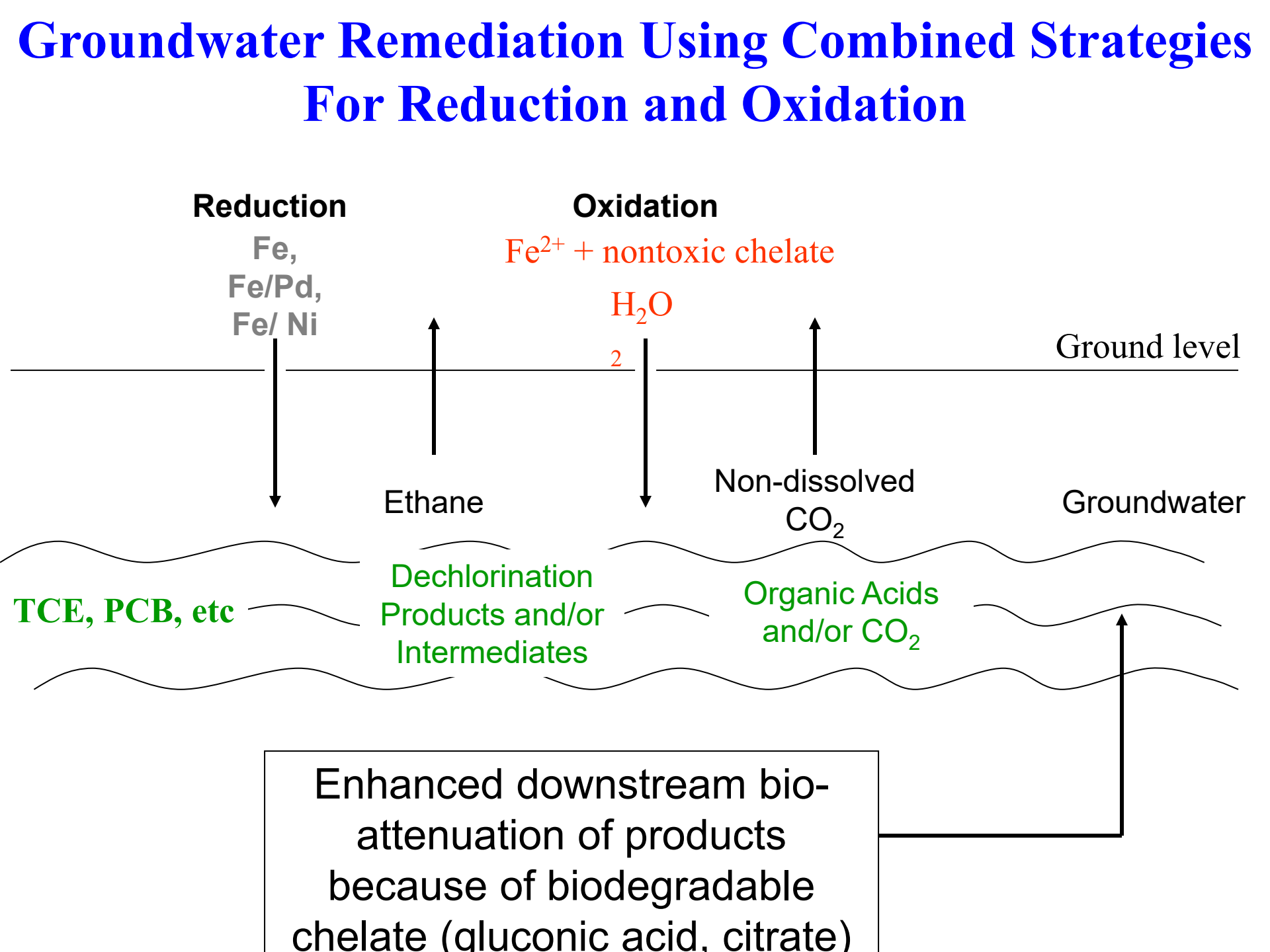
Groundwater

TCE, PCB, etc

Dechlorination
Products and/or
Intermediates

Organic Acids
and/or CO_2

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

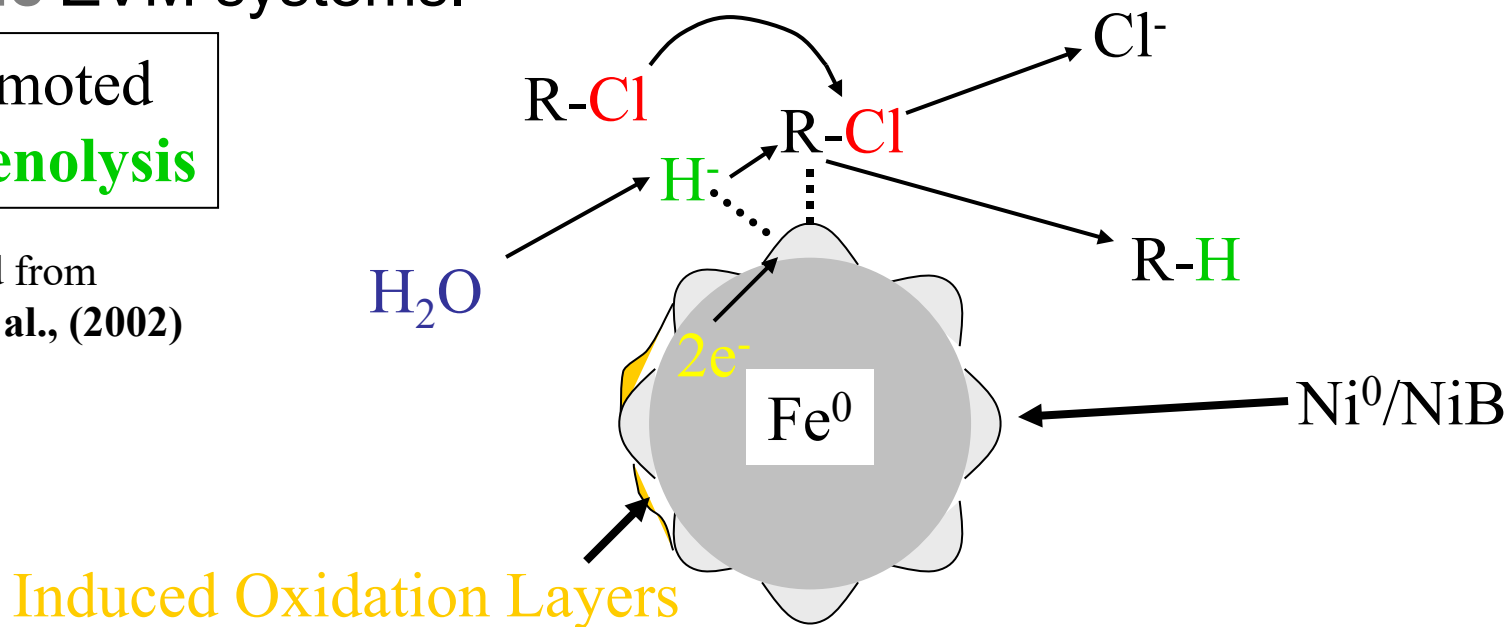


Reductive Dechlorination: Hydrogenolysis and Bimetallic Systems

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

**Ni-Promoted
Hydrogenolysis**

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

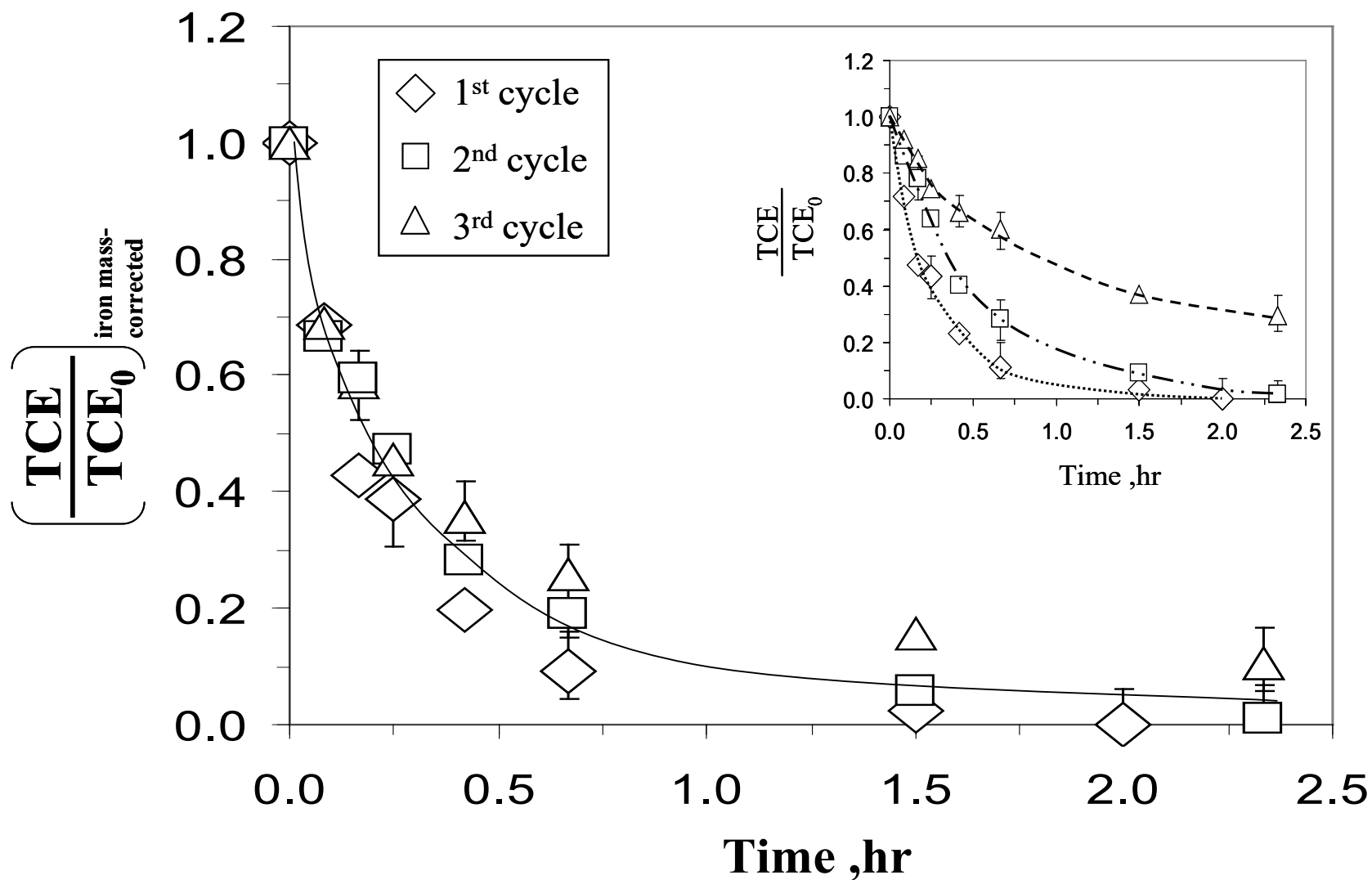


- This mechanism is supported by the fact that dechlorination rates increase as the H-promoting ability of the 2nd metal increases:

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

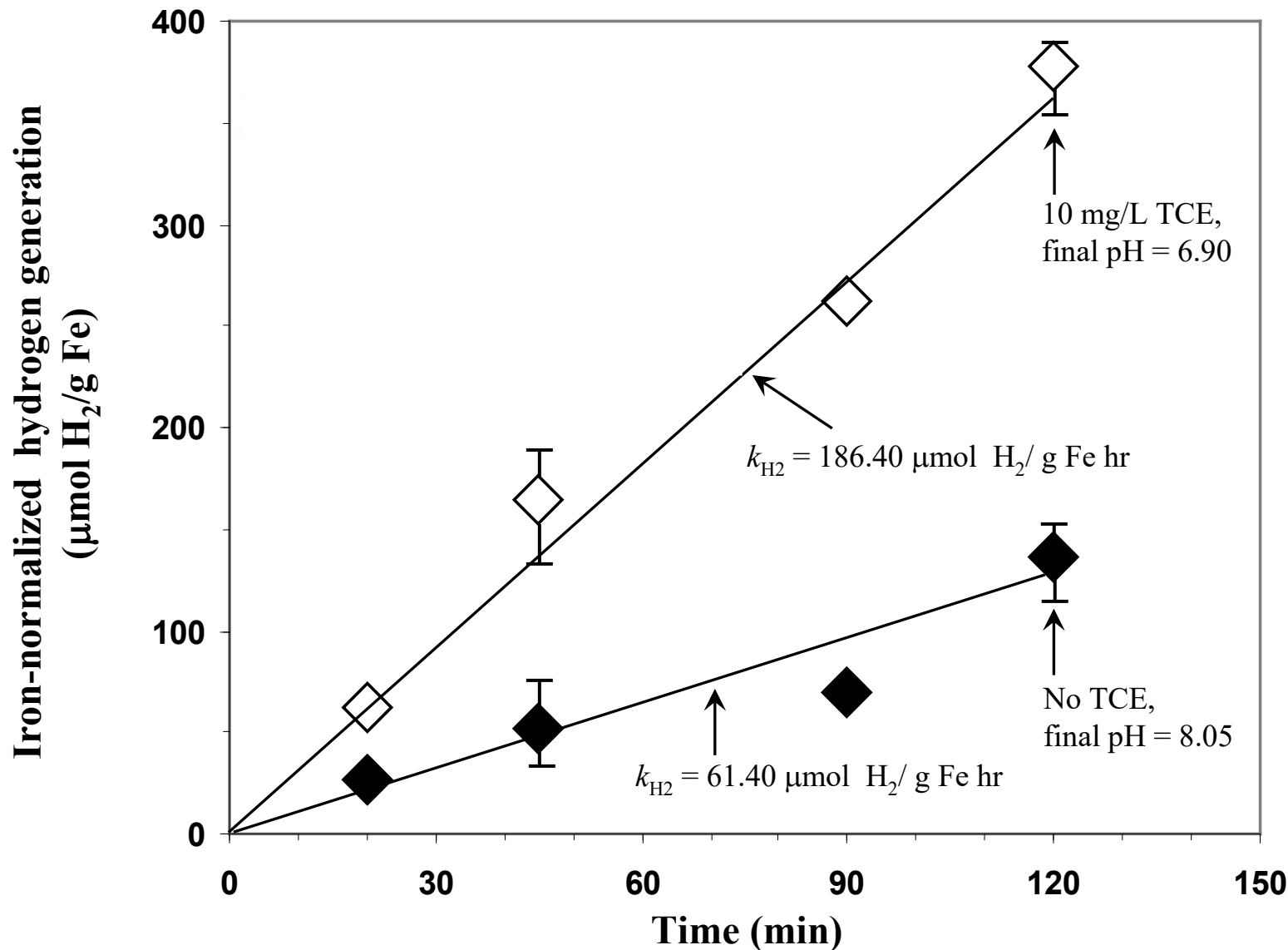
Batch Cycle Study for TCE Degradation by Ni/Fe (Ni = 20 wt%) Nanoparticles in Deoxygenated Water with Headspace:

Metal Loading = 2.5 g/L; pH = 6.5 ; TCE₀ = 10 mg/L



Total H₂ produced as a Function of Time for Ni/Fe (Ni = 20 wt%) Nanoparticles Both With and Without TCE Degradation:

Ni/Fe = 2.5 g/L; pH = 6.5

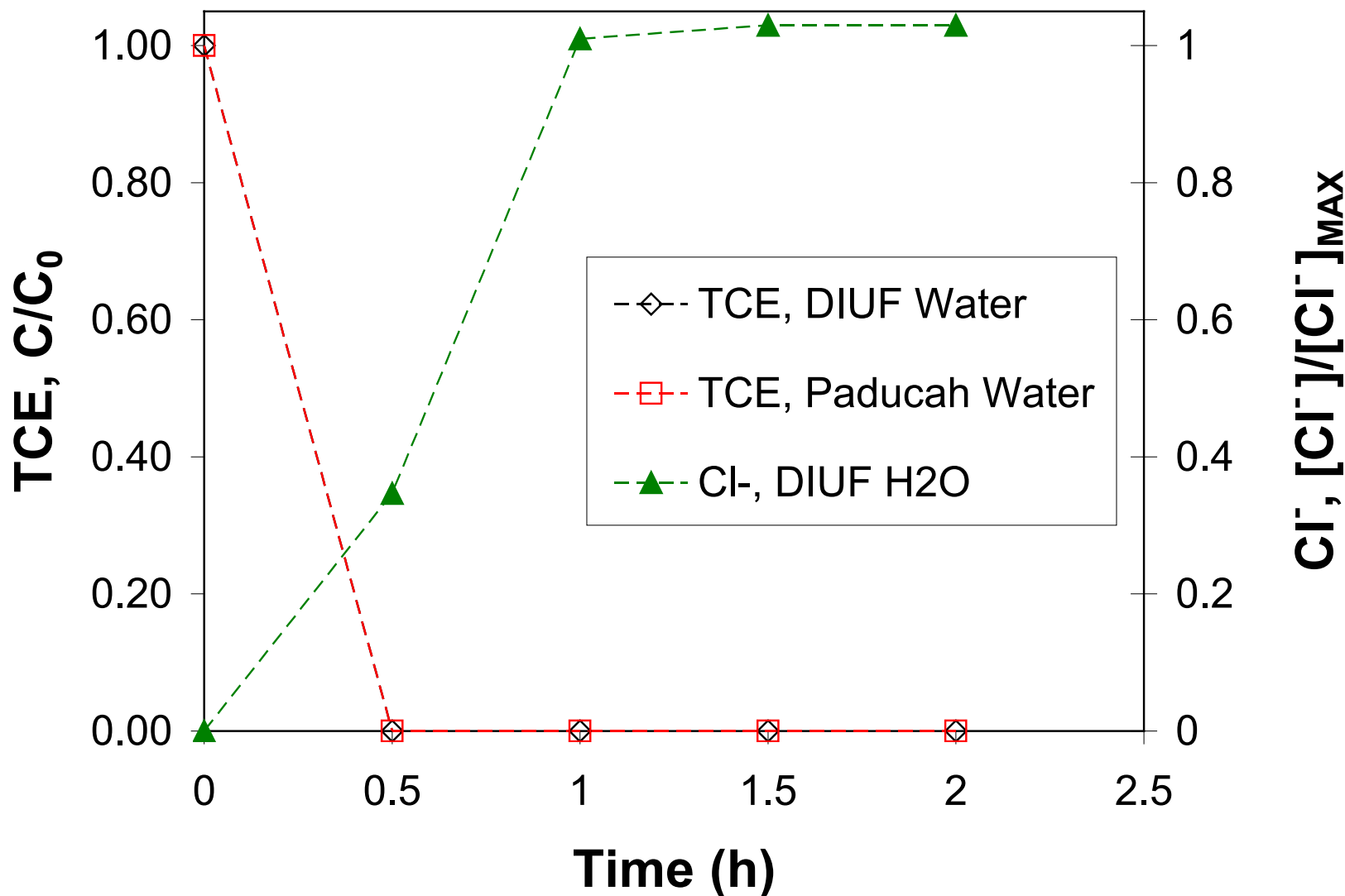


Aspects to Address for Successful TCE Dechlorination Using Direct Injection of Bimetallic Nanoparticle Systems

- 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)

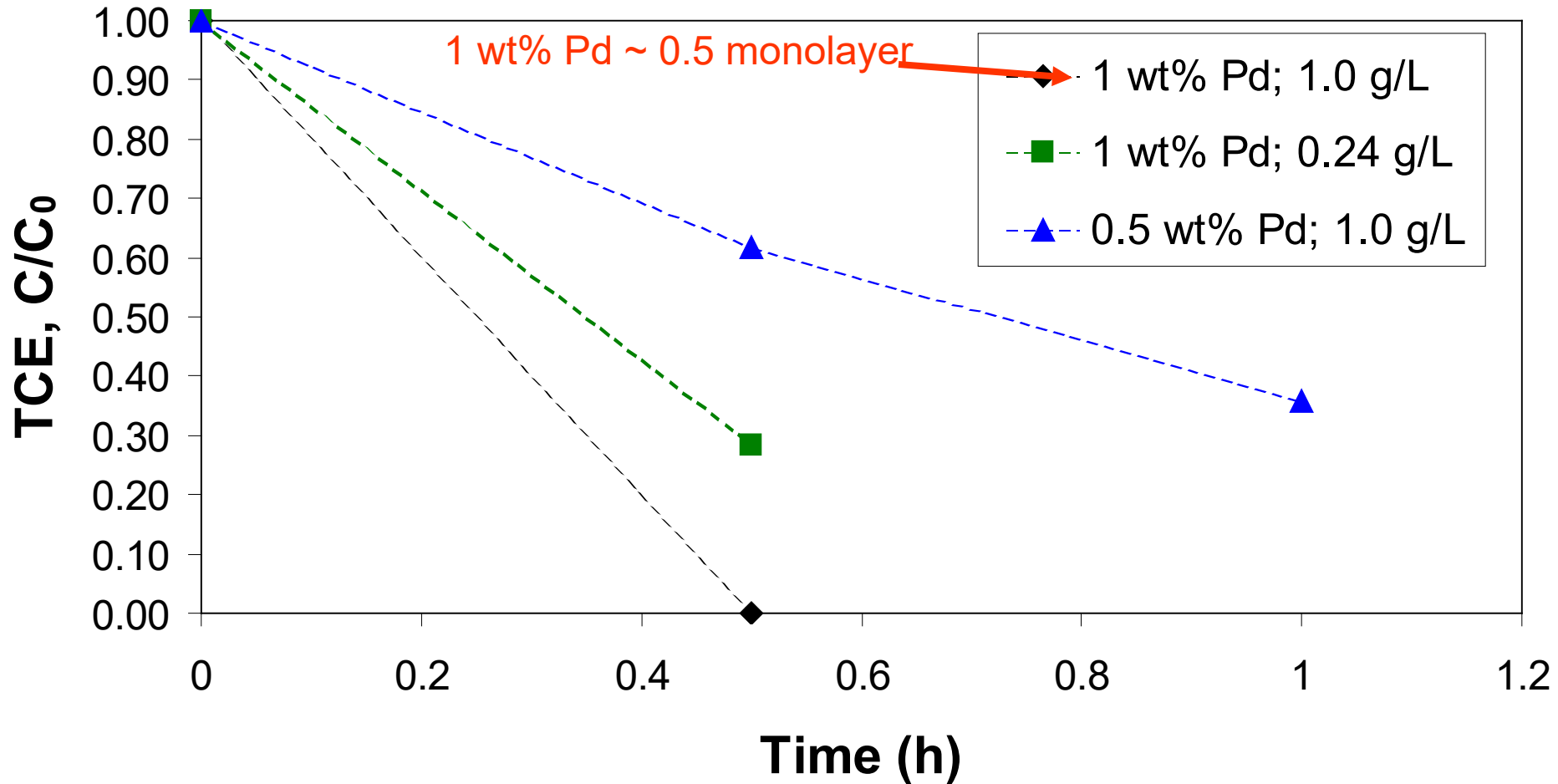
Dechlorination of TCE Using Fe/Pd Nanoparticles (1 wt% Pd) In Deoxygenated Water with Headspace:

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



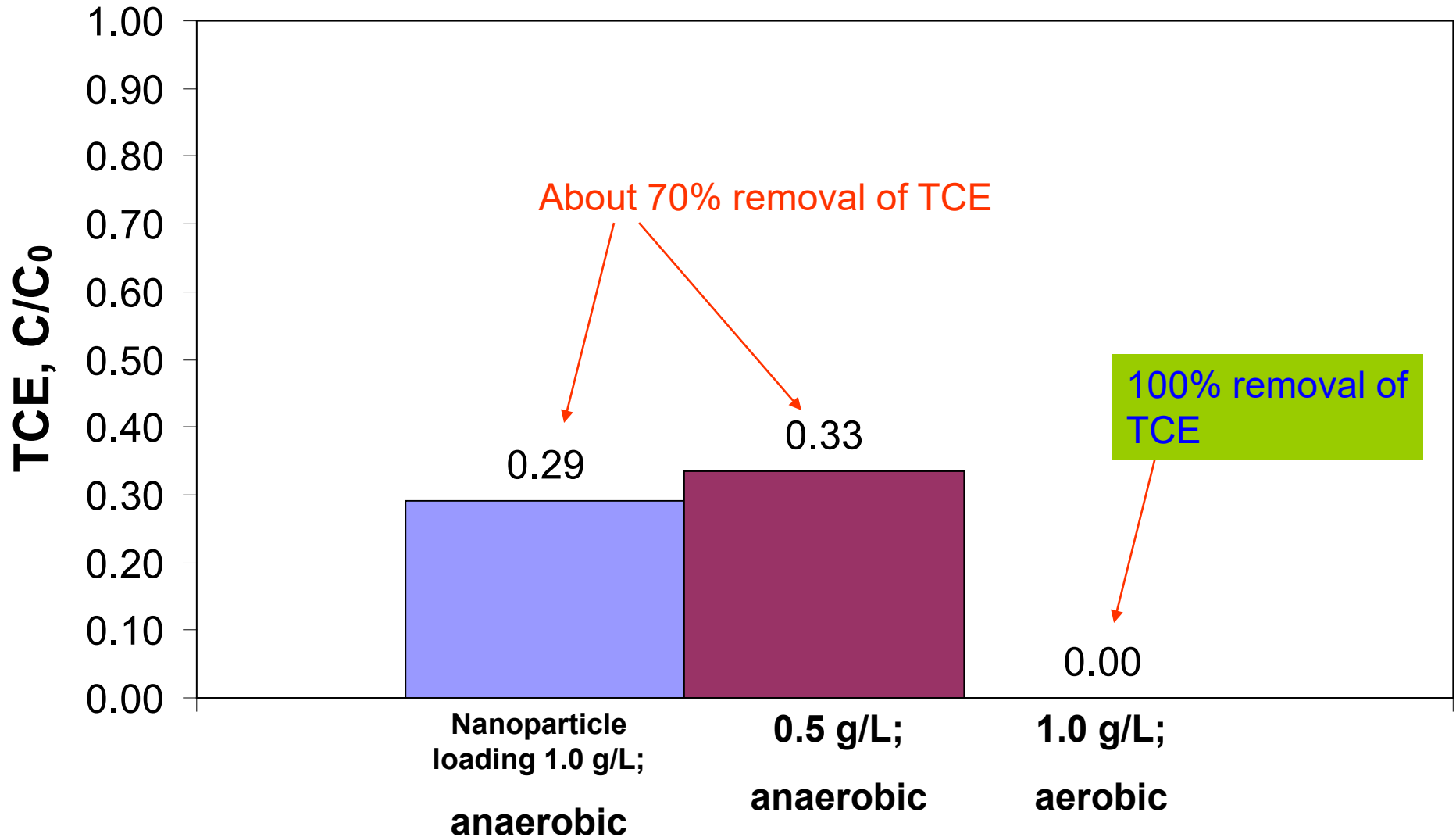
Dechlorination of TCE in Deoxygenated Paducah Water Using Fe/Pd Nanoparticles with Variable Metal Conditions:

$C_0 = 20.5 \text{ mg/L}$; $\text{pH} = 5$



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

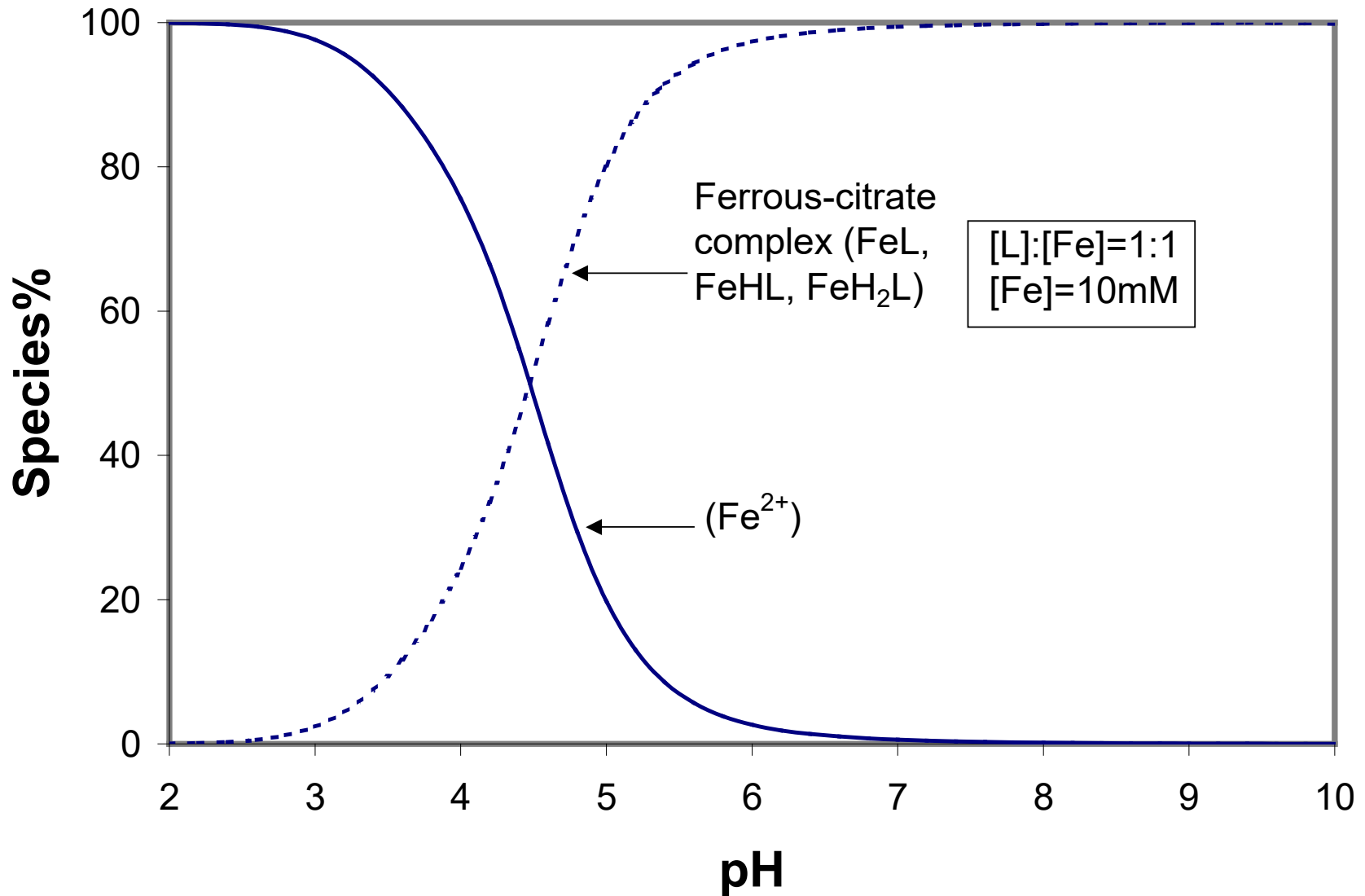
pH = 6; $C_0 = 21.9$ mg/L TCE, Reaction time = 0.5 hr



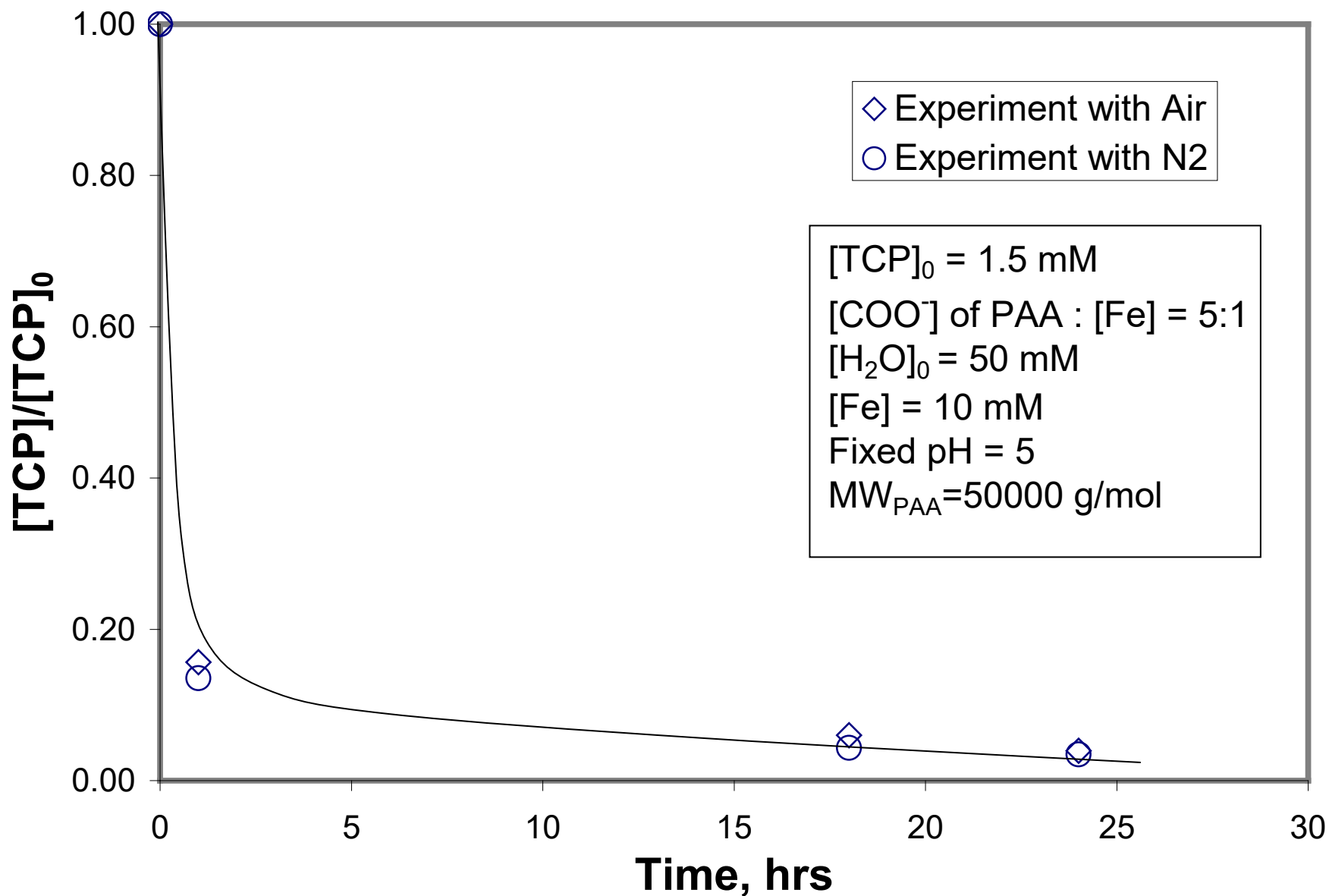
Why Chelate-Based Modified Fenton's Reaction?

- Controlled release of Fe^{2+}
- Prevent Fe(II) oxidation
- At near neutral pH, prevent $\text{Fe}(\text{OH})_3$ 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

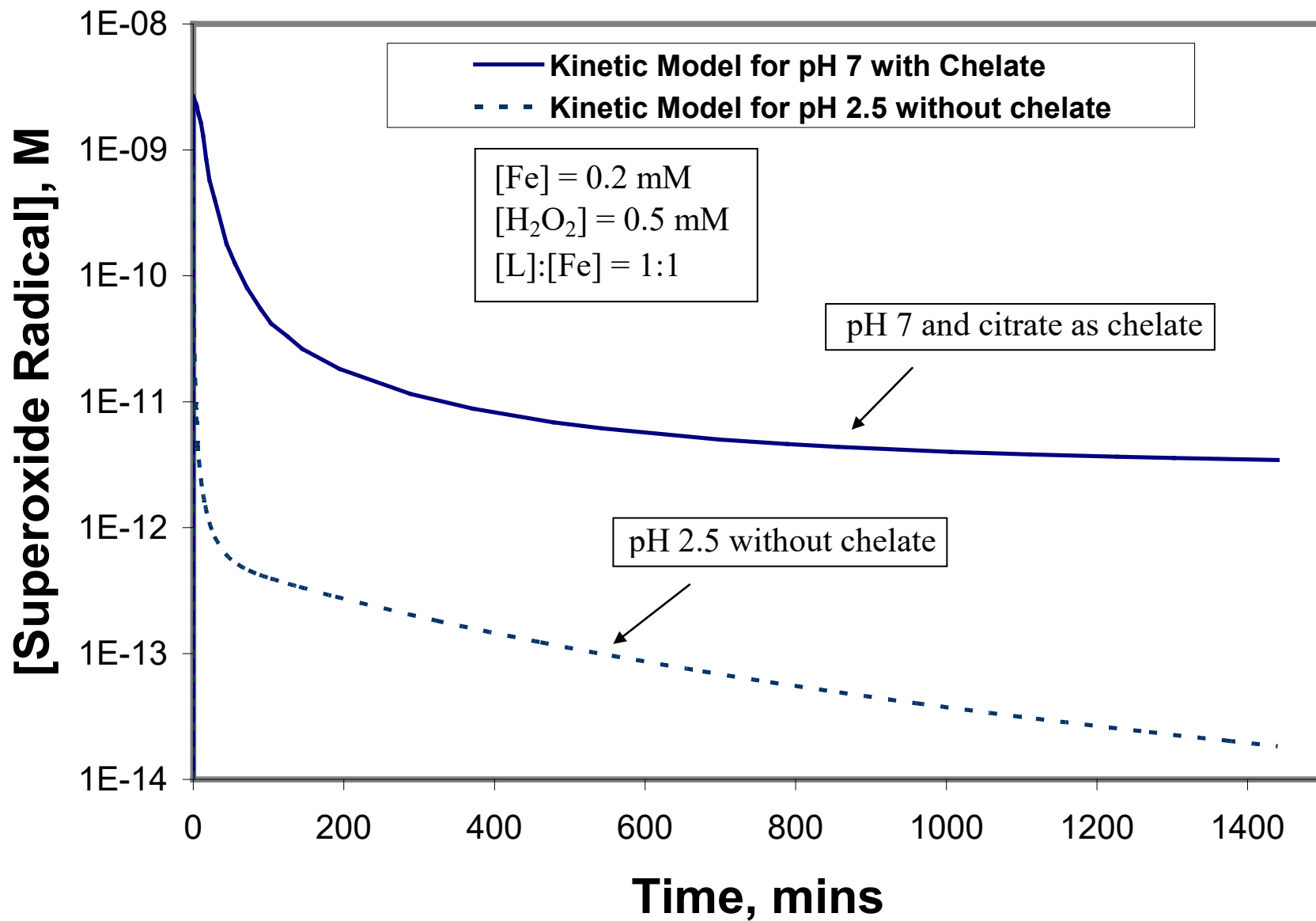
Iron-Citrate Species Distribution



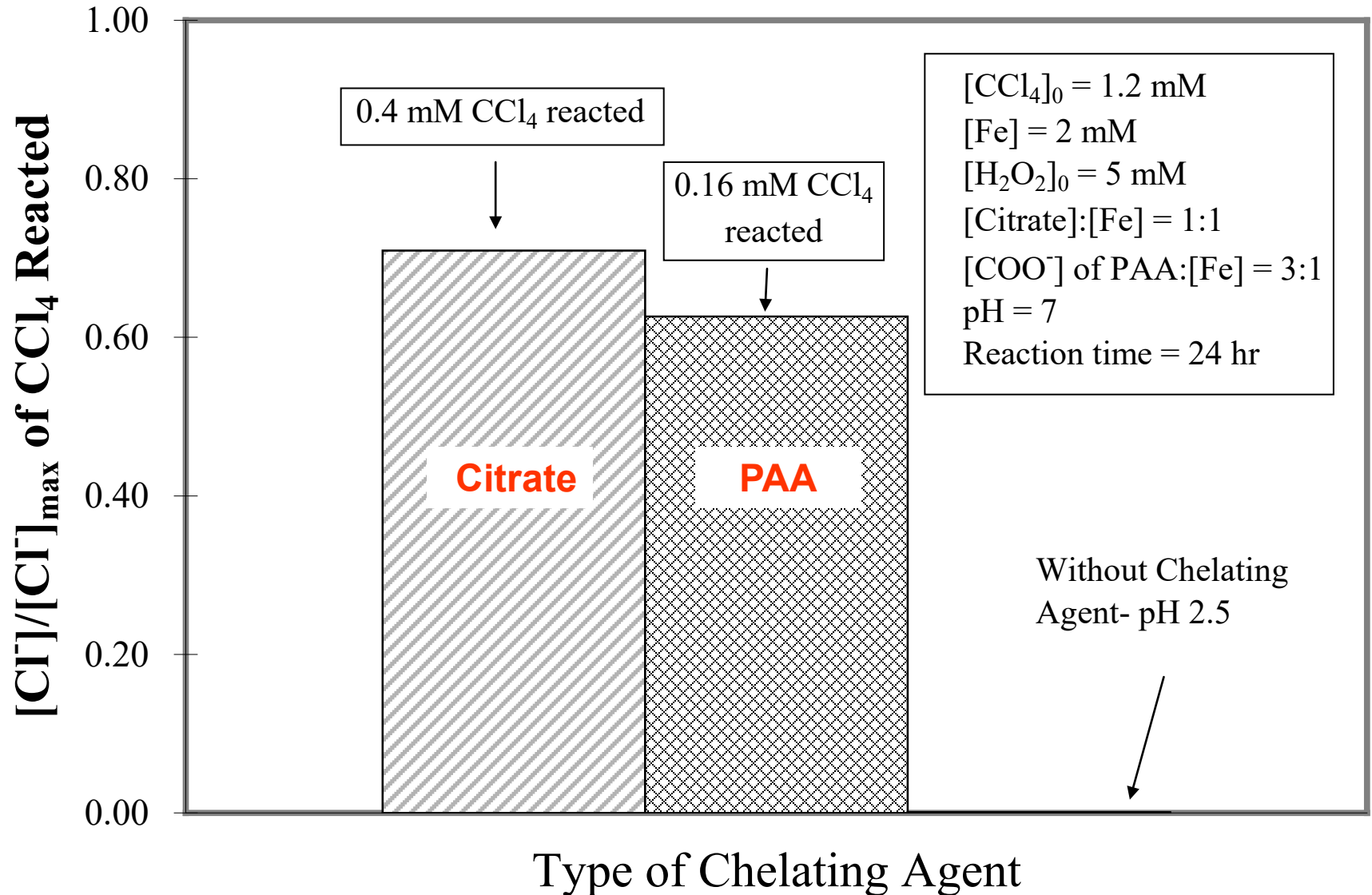
Effect of Dissolved Oxygen for TCP Oxidation by Fe^{2+} + PAA + H_2O_2 System (chelate modified system)



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



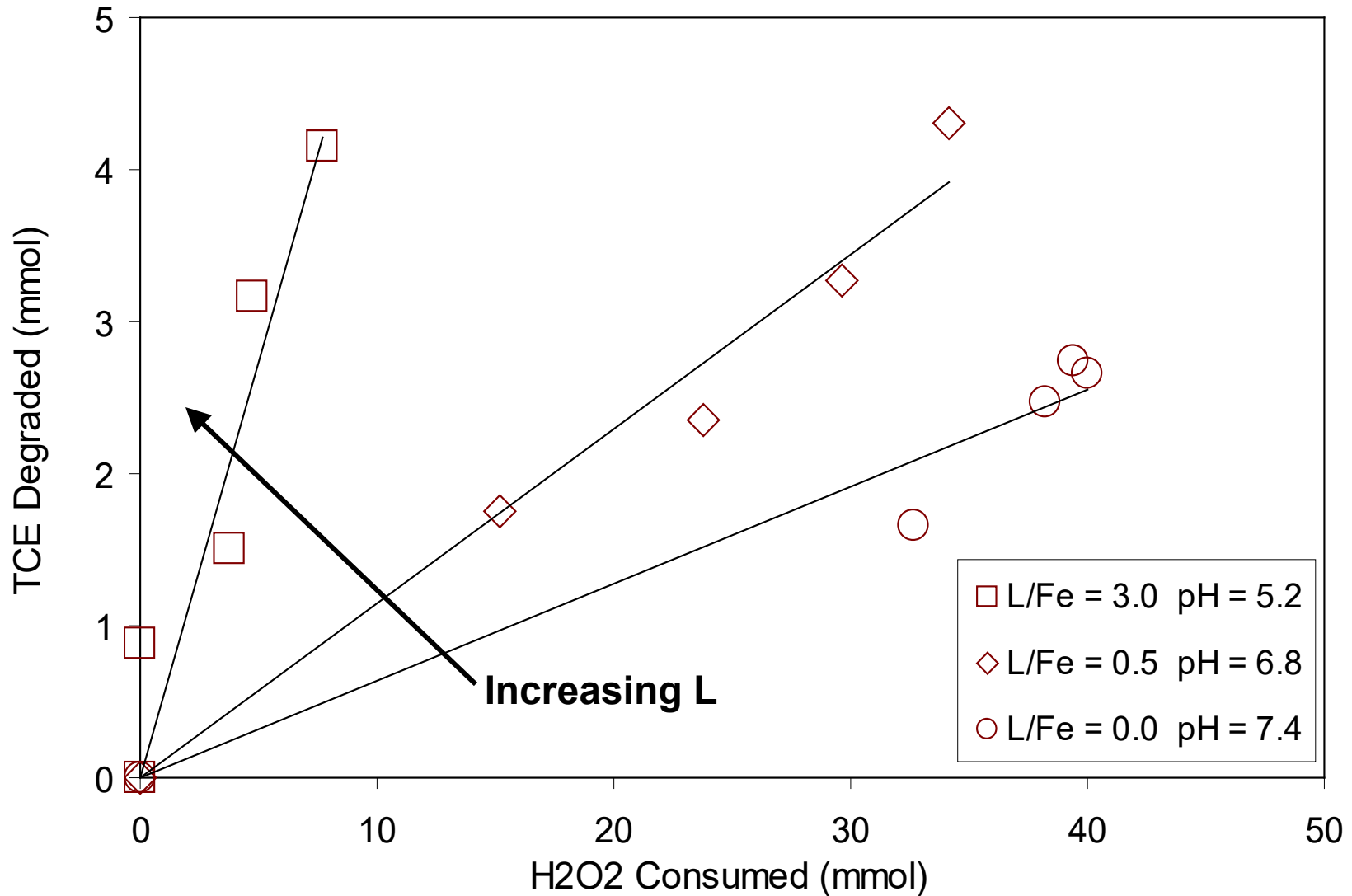
Chloride Formation During CCl_4 dechlorination under Standard and Chelate Based Modified Fenton Reaction at 24 hr Reaction Time



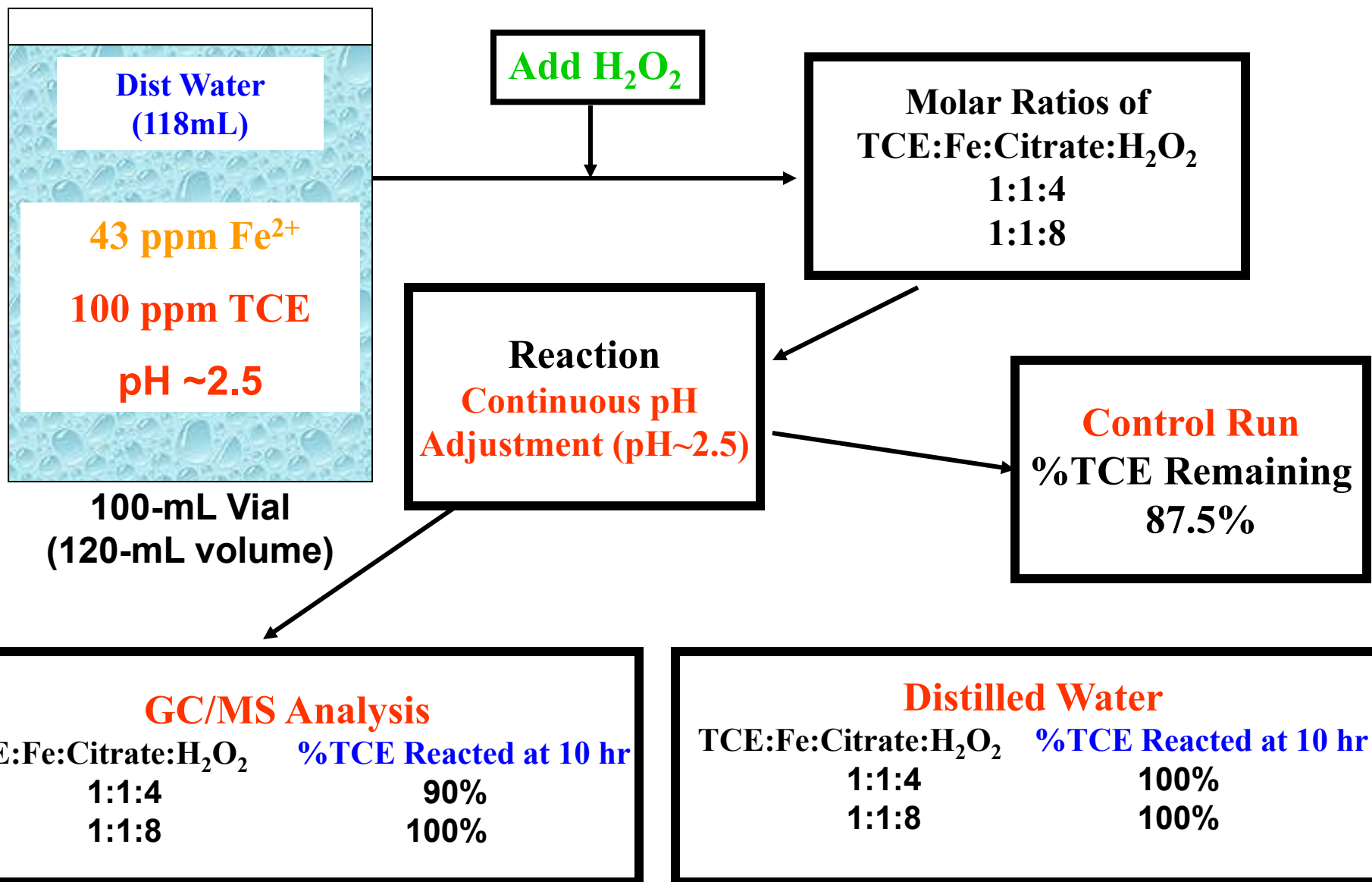
Topics to Address for Successful Dechlorination Using Chelate-Based Modified Fenton's Reaction

- What **reactant ratios** ($[\text{Fe}]:[\text{H}_2\text{O}_2]:[\text{L}]$) 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):H₂O₂ Ratio

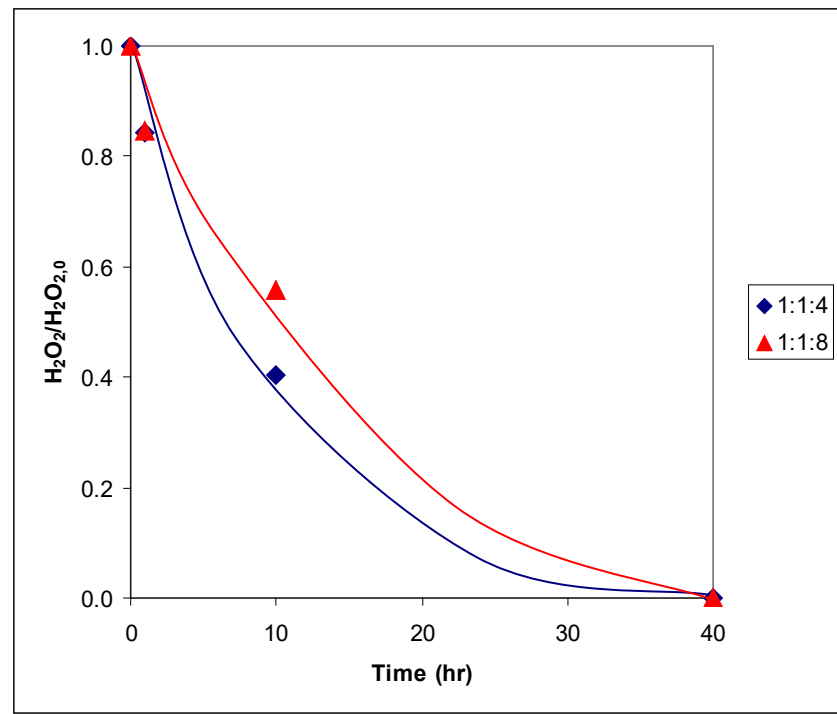
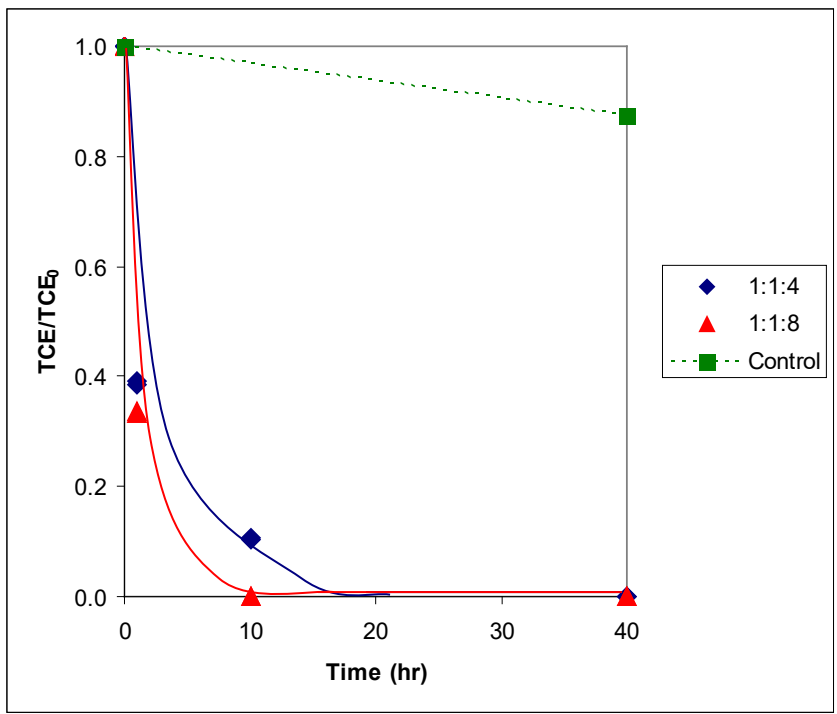


Standard Fenton Reaction (pH=2.5) Using Paducah Water With Varying Fe(II):H₂O₂ Ratio

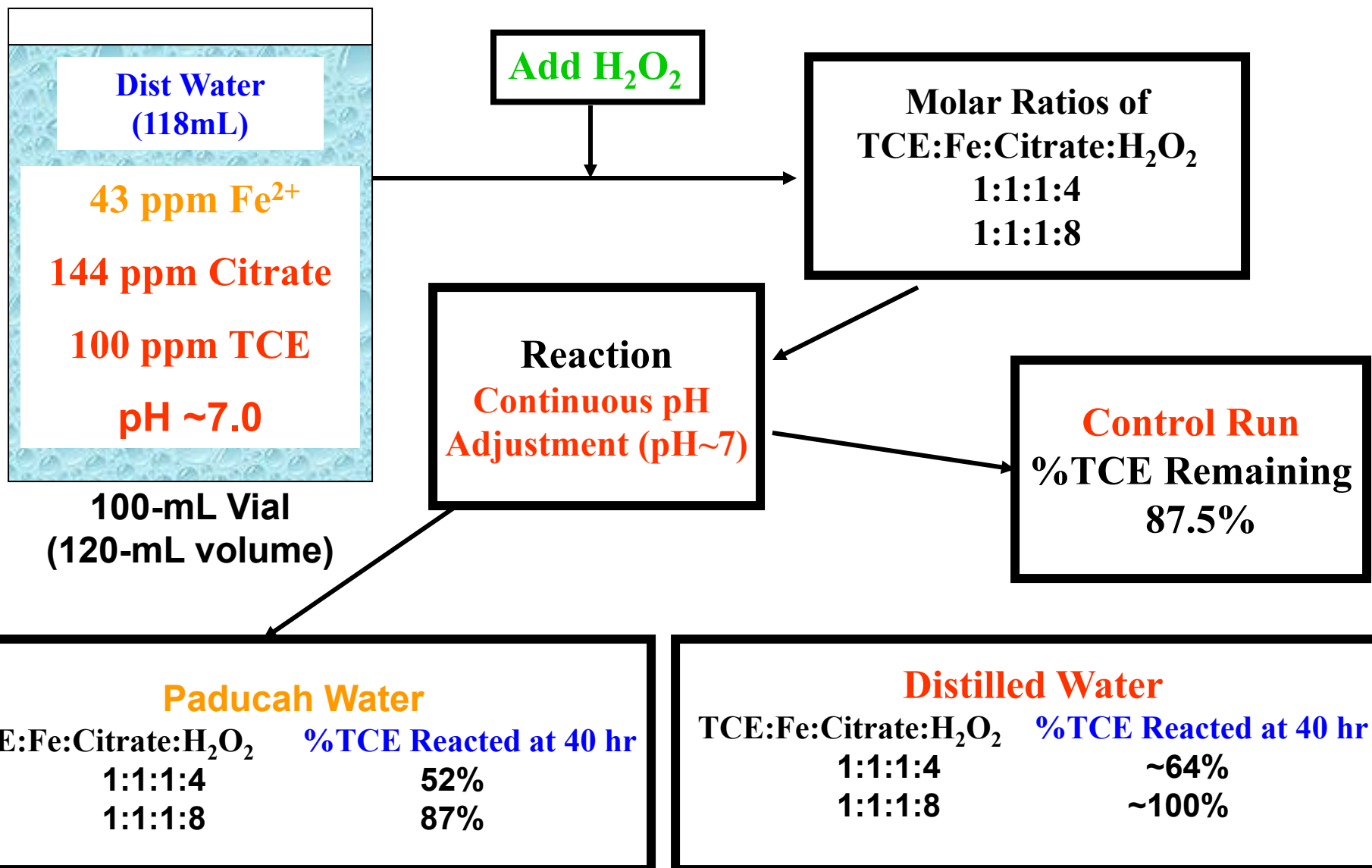
TCE and H₂O₂ concentrations as a function of Time for
TCE:Fe:Citrate:H₂O₂ molar ratios of 1:1:4 and 1:1:8. Initial TCE
concentration of 100ppm.

Control: TCE, Citrate, Fe (no H₂O₂)

Note: Data represents individual runs sampled at indicated time



Modified Fenton Reaction (pH=7.0) Using Paducah Water With Varying Fe(II):H₂O₂ Ratio

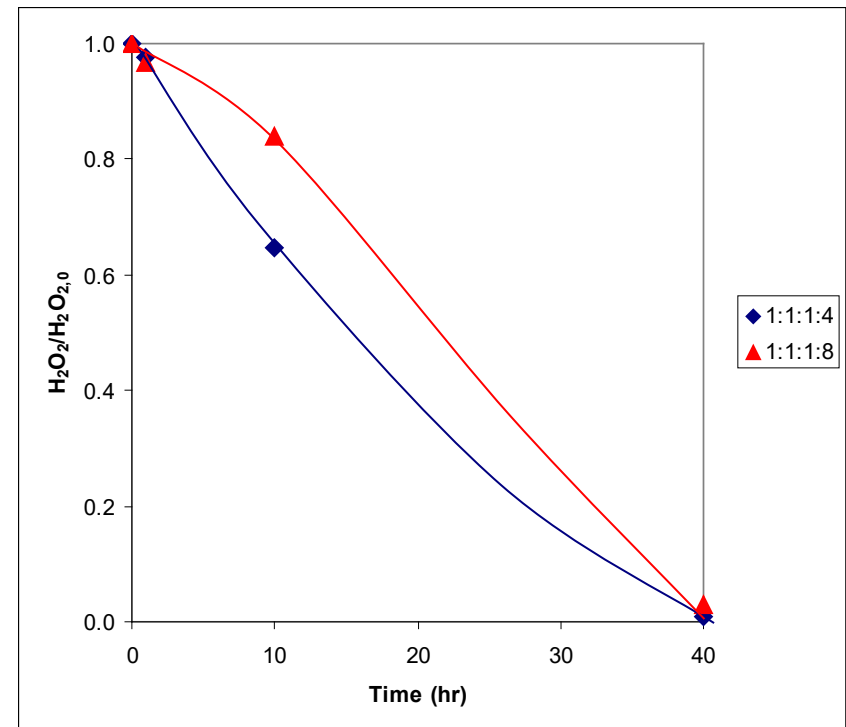
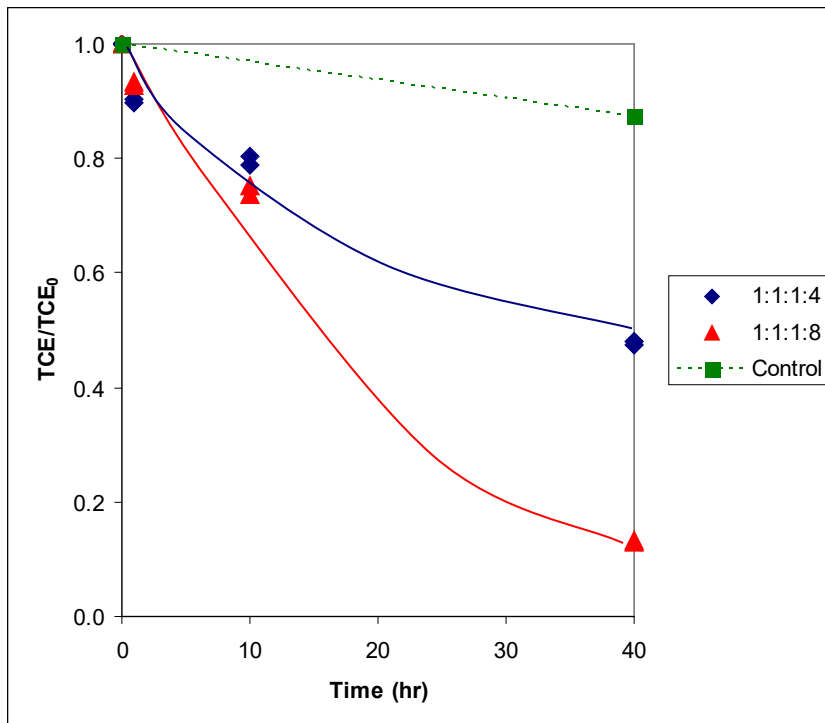


Modified Fenton Reaction (pH=7.0) Using Paducah Water With Varying Fe(II):H₂O₂ Ratio

TCE and H₂O₂ concentrations as a function of Time for
TCE:Fe:Citrate:H₂O₂ molar ratios of 1:1:1:4 and 1:1:1:8. Initial TCE
concentration of 100ppm.

Control: TCE, Citrate, Fe (no H₂O₂)

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 O₂ has minimal impact for the Pd-protected Fe nanoparticles.