Toxic Organic Degradation by Immobilized Nanoparticles and Free Radical Reactions

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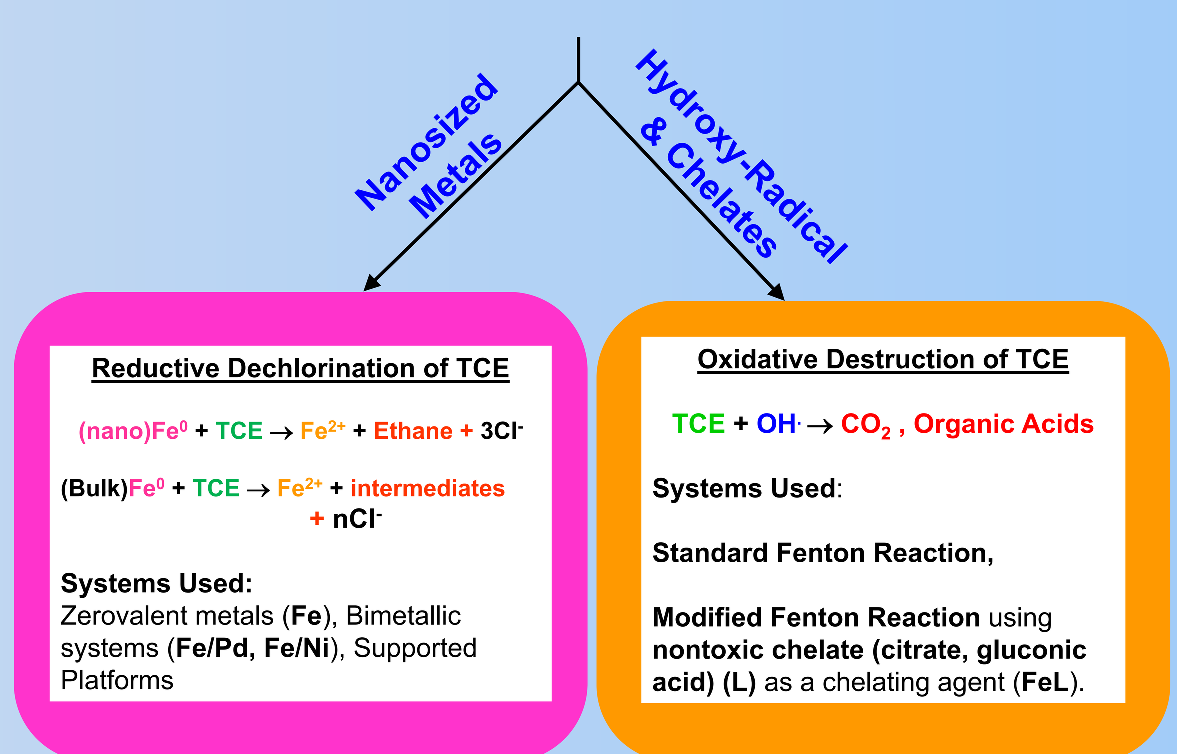
Introduction

Chloro-organics contamination of groundwater and soil is a prevalent concern in various locations. We have successfully evaluated highly effective methods for the destruction of toxic, chlorinated organics through comprehensive mechanistic probing of both oxidative (free-radical reaction pathways) and reductive (zero-valent nanoscale metals) dechlorination systems. For the oxidative pathway, Fe(II), a chelate (citric acid or gluconic acid), and hydrogen peroxide are needed for free radical production. Highly effective dechlorination was obtained with TCE (trichloroethylene in soluble and as DNAPL form), and selected PCBs. Because of the diversity of chemicals present in hazardous waste and Superfund sites, the development of integrated, cost-effective technologies (both oxidative and reductive systems) is important for solving various remediation problems.

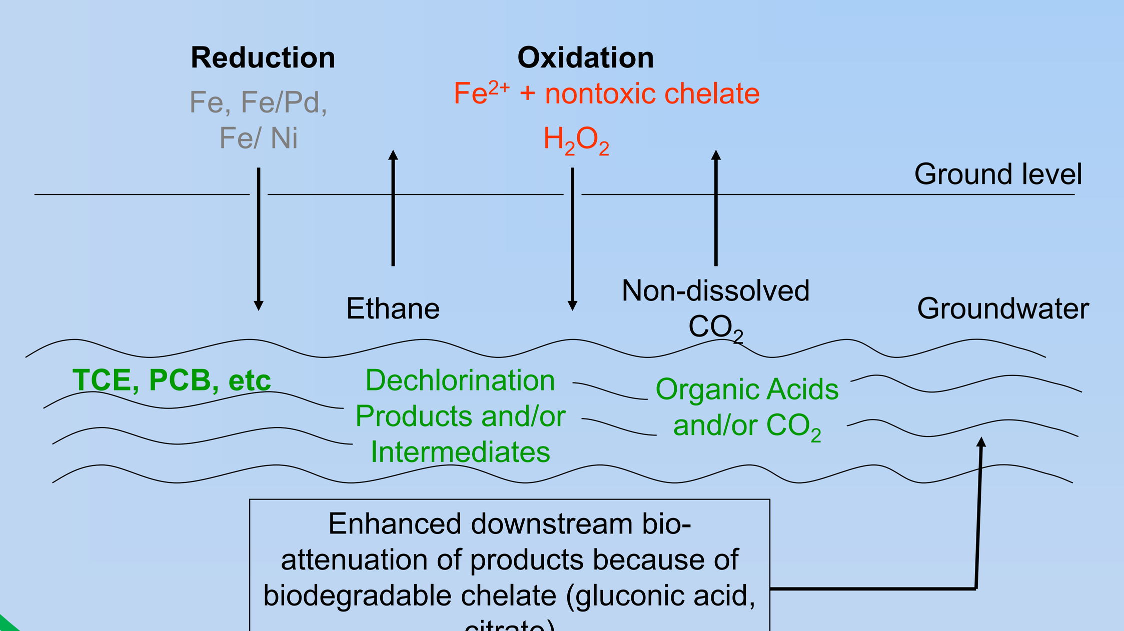
Objectives

- Development of **effective methods** for the dechlorination of toxic organics
- Determine role of **dopant metal** in bimetallic nanoparticle reactivity
- Study potential for **on-site generation** of chemicals needed for chelate-modified Fenton reaction
- Determine effectiveness of both **reductive and oxidative dechlorination** in column studies to simulate groundwater flow

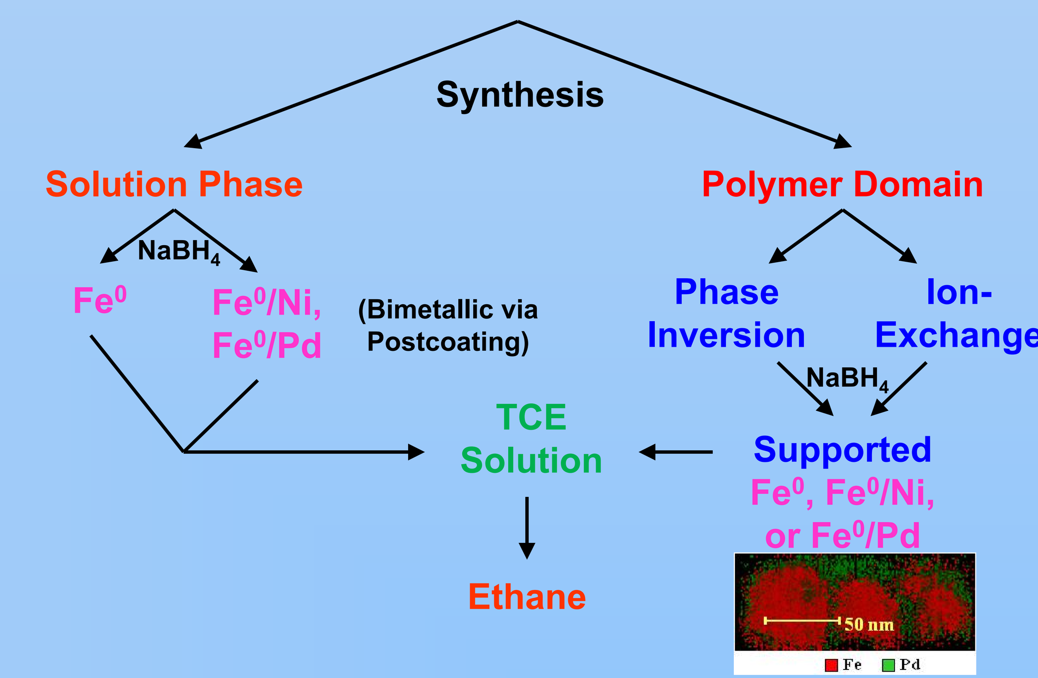
Removal of TCE at Ambient Temperature



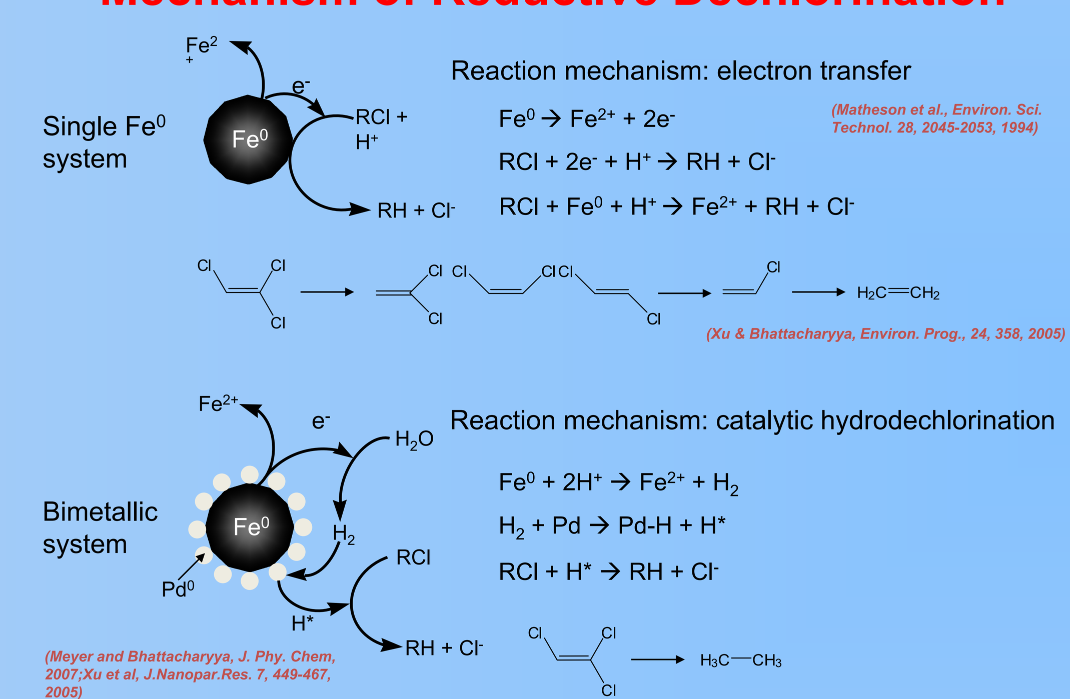
Groundwater Remediation Using Combined Strategies For Reduction and Oxidation



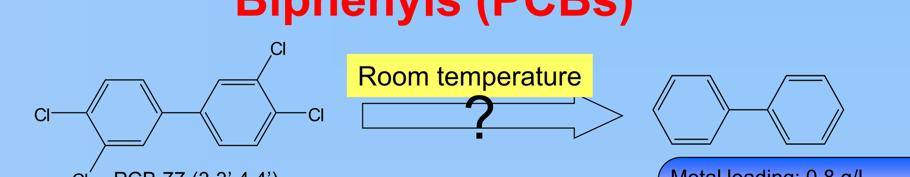
Reductive Dechlorination of TCE

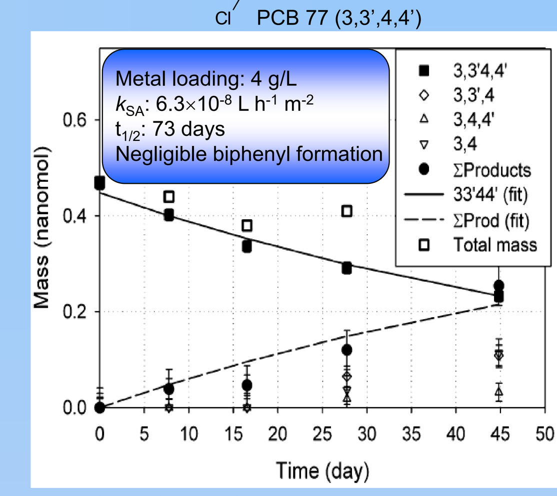


Mechanism of Reductive Dechlorination

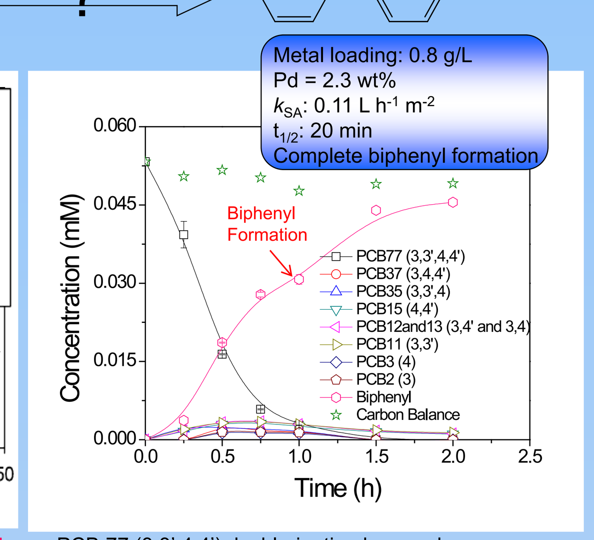


Reductive Dechlorination of Polychlorinated Biphenyls (PCBs)



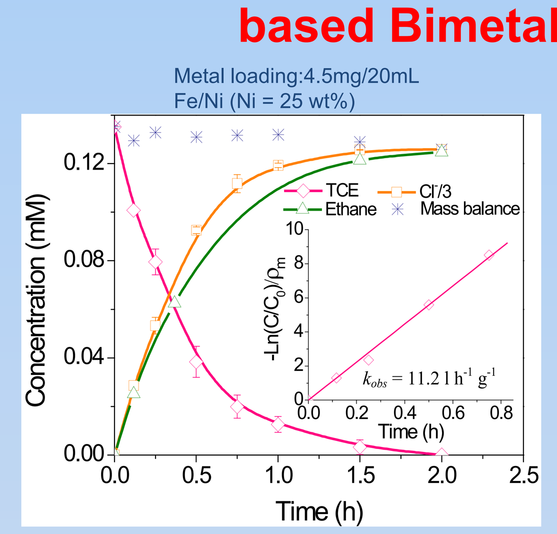


PCB 77 (3,3',4,4') dechlorination by Fe nanoparticles at room temperature (from *Lowry, et al., Environ. Sci. Technol. 2004, 38, 5208*)

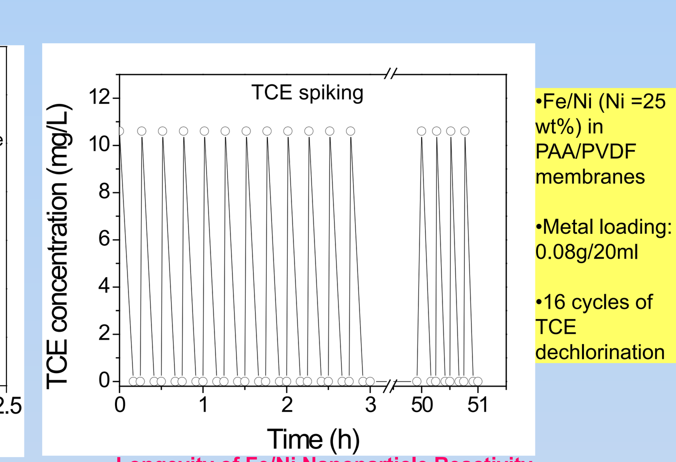


PCB 77 (3,3',4,4') dechlorination by membrane based Fe/Pd (Pd=2.3 wt%) nanoparticles at room temperature

Reductive Dechlorination of TCE by Membrane-based Bimetallic Nanoparticles

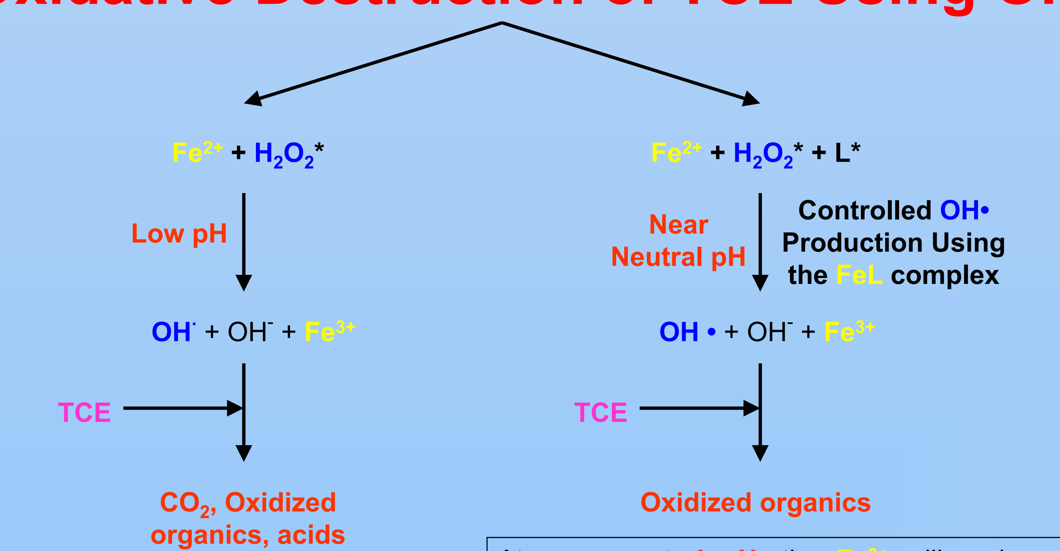


Fast and complete degradation



Longevity of Fe/Ni Nanoparticle Reactivity

Oxidative Destruction of TCE Using OH•



At near neutral pH, the Fe^{2+} will undergo complexation as FeL. This slows OH• production and prevents Fe(III) hydroxide pptn

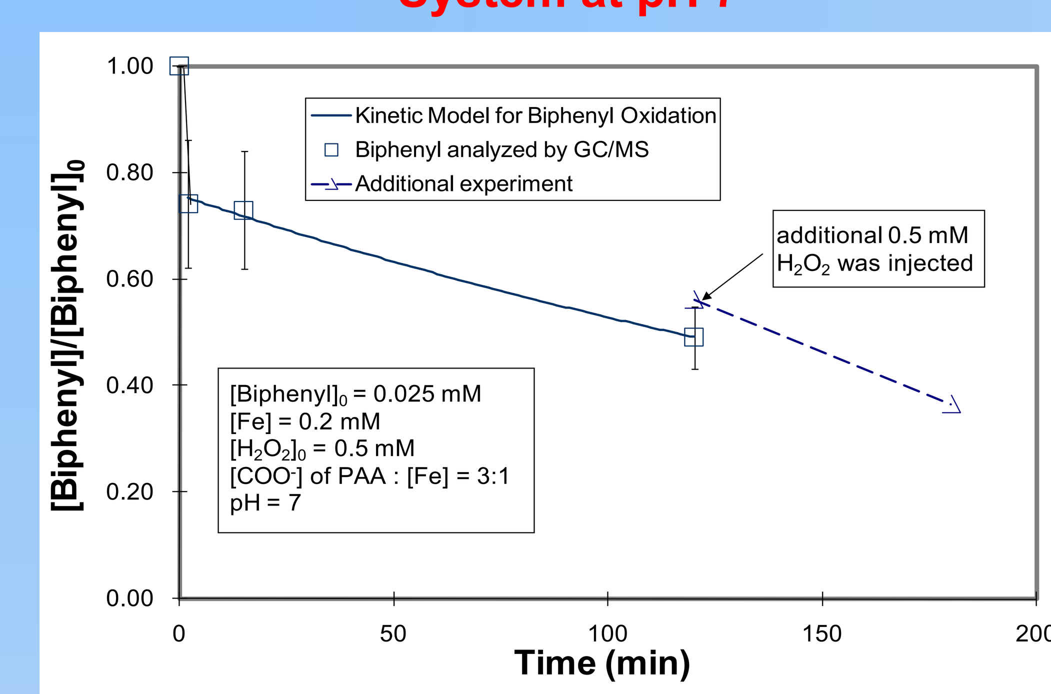
Required Chemicals for Chelate-Based Modified Fenton Reaction

Citrate

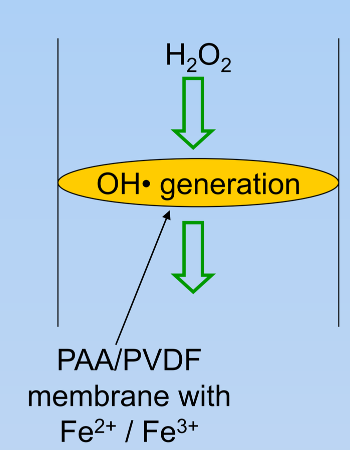
Ferrous Sulfate

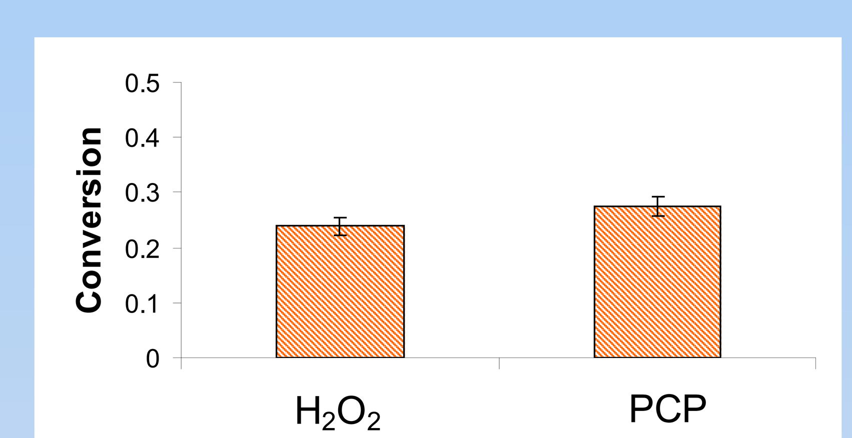
Hydrogen Peroxide

Biphenyl Oxidation by Fe^{2+} + H_2O_2 + PAA System at pH 7



Catalyzed H_2O_2 Propagations by Membrane-Immobilized Fe Ions

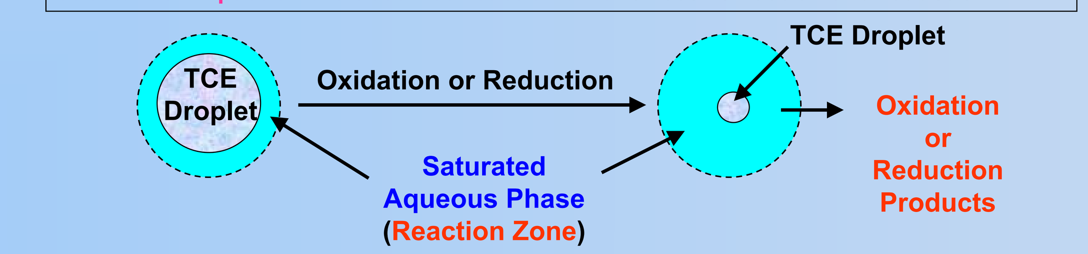




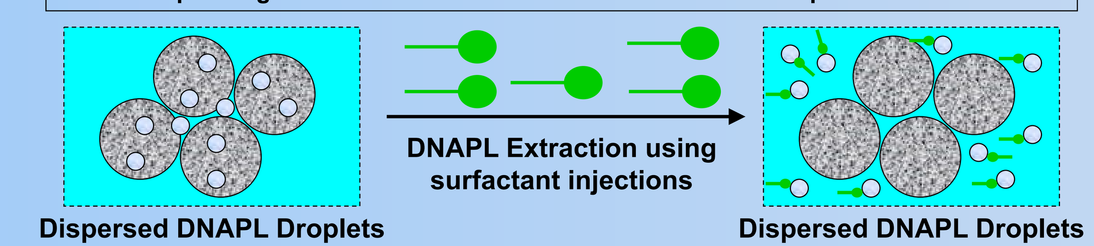
H_2O_2 and PCP conversion for membrane-immobilized Fenton reaction with 22 μmol of captured Fe(III) at pH = 6. Feed contains 150 μmol/L H_2O_2 and 20 μmol/L PCP. τ = 60 ± 2 s, water permeability = 1.7 × 10^{-4} cm^3 cm^{-2} bar^{-1} s^{-1}.

The Challenges of DNAPLs

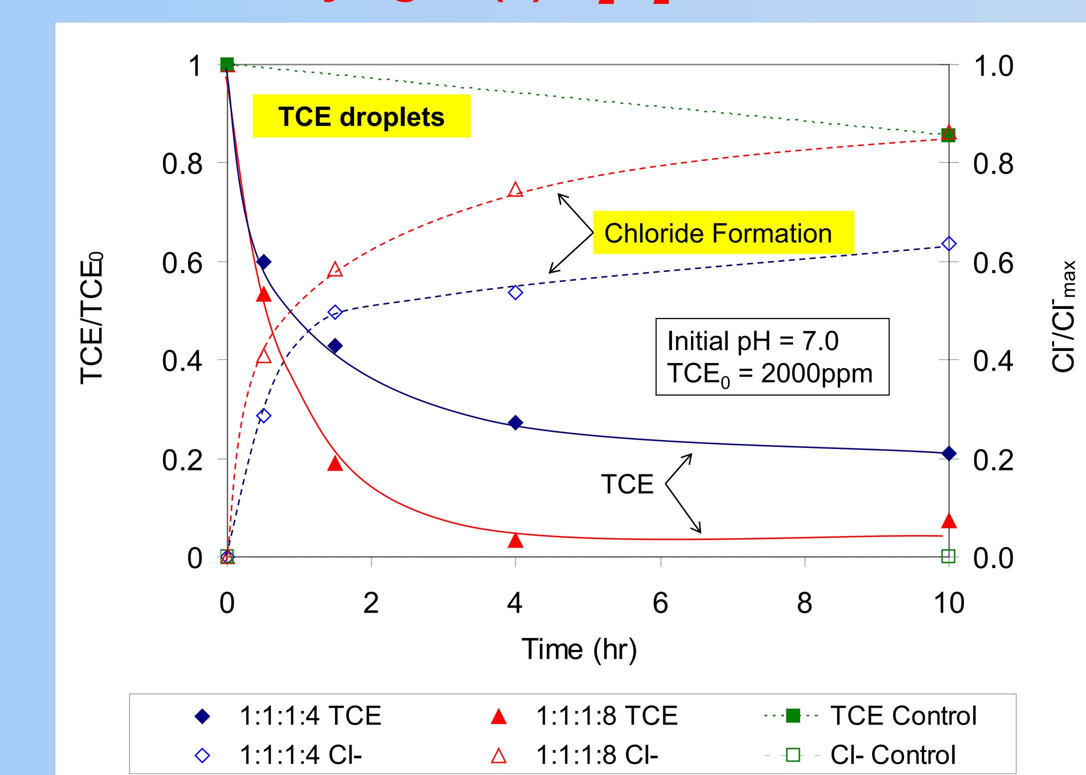
1.) TCE droplets dispersed in the aqueous phase will act as a source of TCE and shrink as mass is lost to the aqueous phase. The mass transfer between phases may have substantial impact on the observed reaction time for both oxidation and reduction.



2.) If DNAPL droplets are dispersed within soil and rock, they may require much greater reaction times for direct treatment. To overcome this problem, surfactant addition can potentially be used to mobilize the DNAPL from the sediment. Laboratory packed columns operating under trickle-flow can be used to examine this phenomenon.



Chelate-Modified Fenton Reaction Using DIUF Water with TCE DNAPL and Varying Fe(II):H_2O_2 Molar Ratio



Conclusions

- Demonstrated fast and **complete dechlorination** of **TCE and selected PCBs** by nanomaterial-based reductive process. Demonstrated further breakdown of biphenyl by chelate-modified Fenton reaction.
- Developed an in-situ polymerization functionalization method to enhance the metal capture and immobilization as well as the **control of nanoparticle size** and distribution through high loading of ion-exchange groups inside membrane pores.
- Quantified the role of **dopant metal** (Pd) and the effect of dopant coating content in terms of bimetallic nanoparticle reactivity.
- Demonstrated **TCE-DNAPL** could be dechlorinated by chelate-modified Fenton reaction at neutral pH environment.
- Achieved controllable degradation of PCP using the Fenton reaction immobilized within PAA/PVDF membrane pores
- Both oxidative and nanotechnology-based treatments of TCE in a simulated groundwater column demonstrated > 50% TCE removal using **minimal chemical dosing**.

Acknowledgement

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