Degradation of Toxic Organics by Nanosized Metallic Systems and by Hydroxyl Radical Reaction

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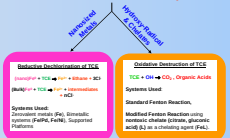
Introduction

Chloro-organics contamination of groundwater and soil is quite widespread 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.

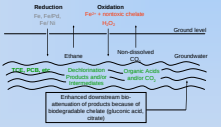
Objectives

- 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

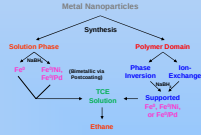
Removal of TCE at Ambient Temperature



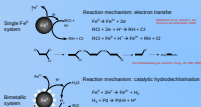
Groundwater Remediation Using Combined Strategies For Reduction and Oxidation



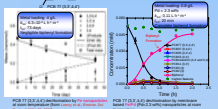
Reductive Dechlorination of TCE



Mechanism of Reductive Dechlorination



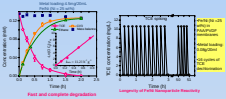
Reductive Dechlorination of Polychlorinated Biphenyls (PCBs)



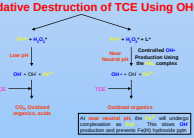
PCB-77 (3,3',4,4'-) dechlorination by Fe nanoparticles at room temperature (from Lowry et al., Environ. Sci. Technol. 2004, 38, 5461)

PCB-77 (3,3',4,4') dechlorination by membrane bound Ni/Fe (PdO-2.3 wt%) nanoparticles at room temperature

Reductive Dechlorination of TCE by Membrane-based Bimetallic Nanoparticles



Oxidative Destruction of TCE Using OH•



At near neutral pH, the will undergo complexation as This slows OH production and prevents Fe(III) hydroxide ppt.

Required Chemicals for Chelate-Based Modified Fenton Reaction

Citrate

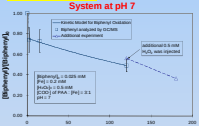
Ferrous Sulfate

Hydrogen Peroxide

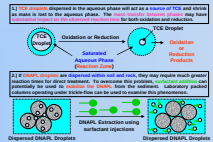
Technology Enhancement: On-site Generation of Chelate and H_2O_2

Gluconic acid produced by enzymatic reaction would act as a chelate in Fenton reaction, and thus allow degradation of TCE & PCBs near neutral pH

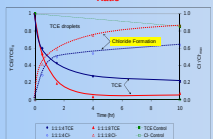
Biphenyl Oxidation by Fe^{2+} + H_2O_2 + PAA System at pH 7



The Challenges of DNAPLs



Chelate-Based Fenton Reaction (initial pH=7.0) Using DIUF Water with DNAPL (2000ppm TCE) 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.
- Both oxidative and nanotechnology-based treatments of TCE in column studies simulating groundwater flow demonstrated >50% TCE removal using **minimal chemical dosing.**

Acknowledgement

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