Nanotechnology for Treatment of Contaminated Water

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Detoxification of Chloro-Organics, such as TCE, PCB (At Room Temperature)

Nanosized Metals

Hydroxy-Radical & Chelates

Reduction pathway for Chlorinated Compounds

PCB → Biphenyl
TCE → Ethane

Systems:
Zerovalent metals (Fe),
Bimetallic system (Fe/Pd, Fe/Ni), Polymer Platform

Combined Pathway

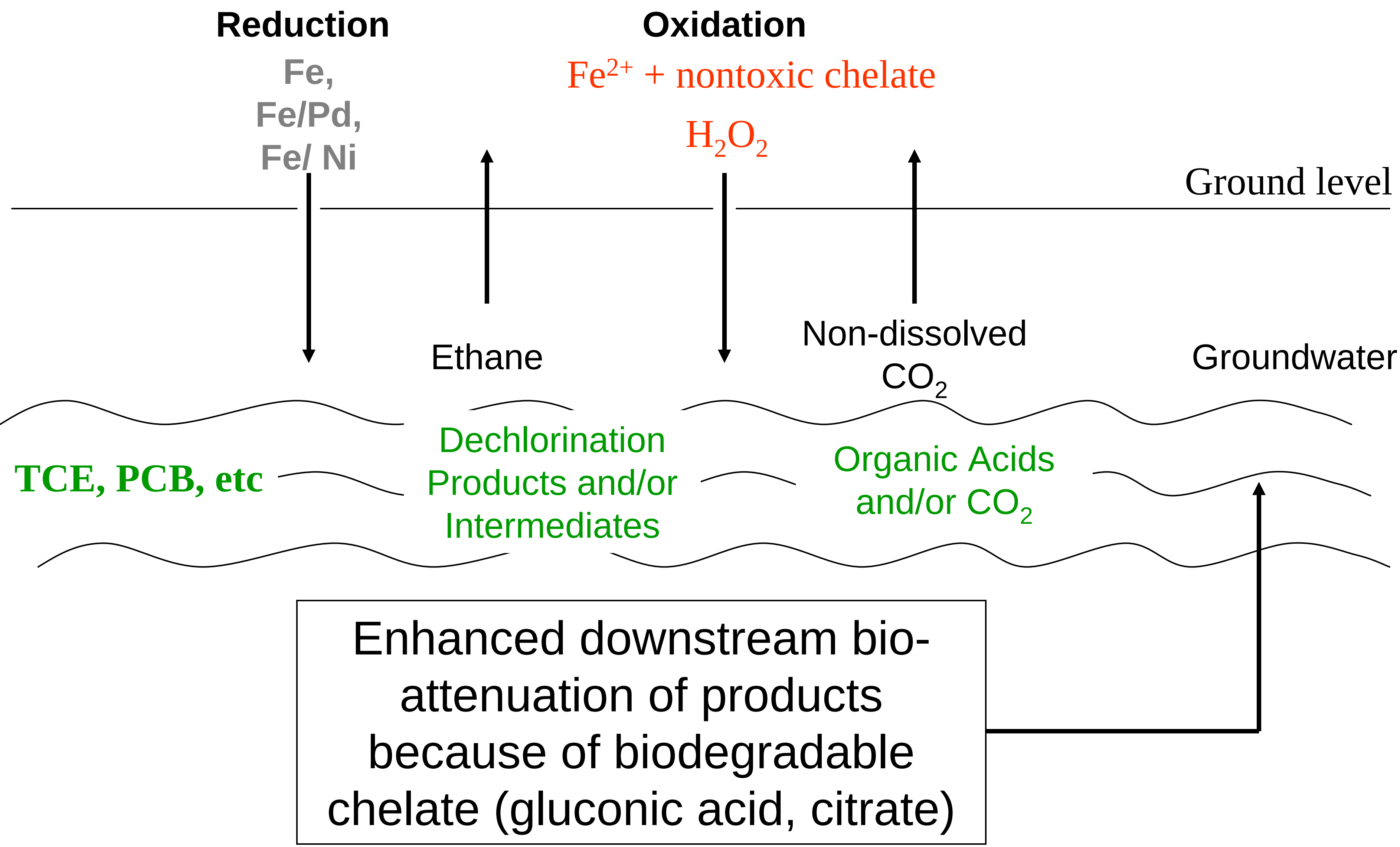
Oxidation of Chlorinated Compounds

Products: CO_2, Organic Acids, Potential chloro-intermediates

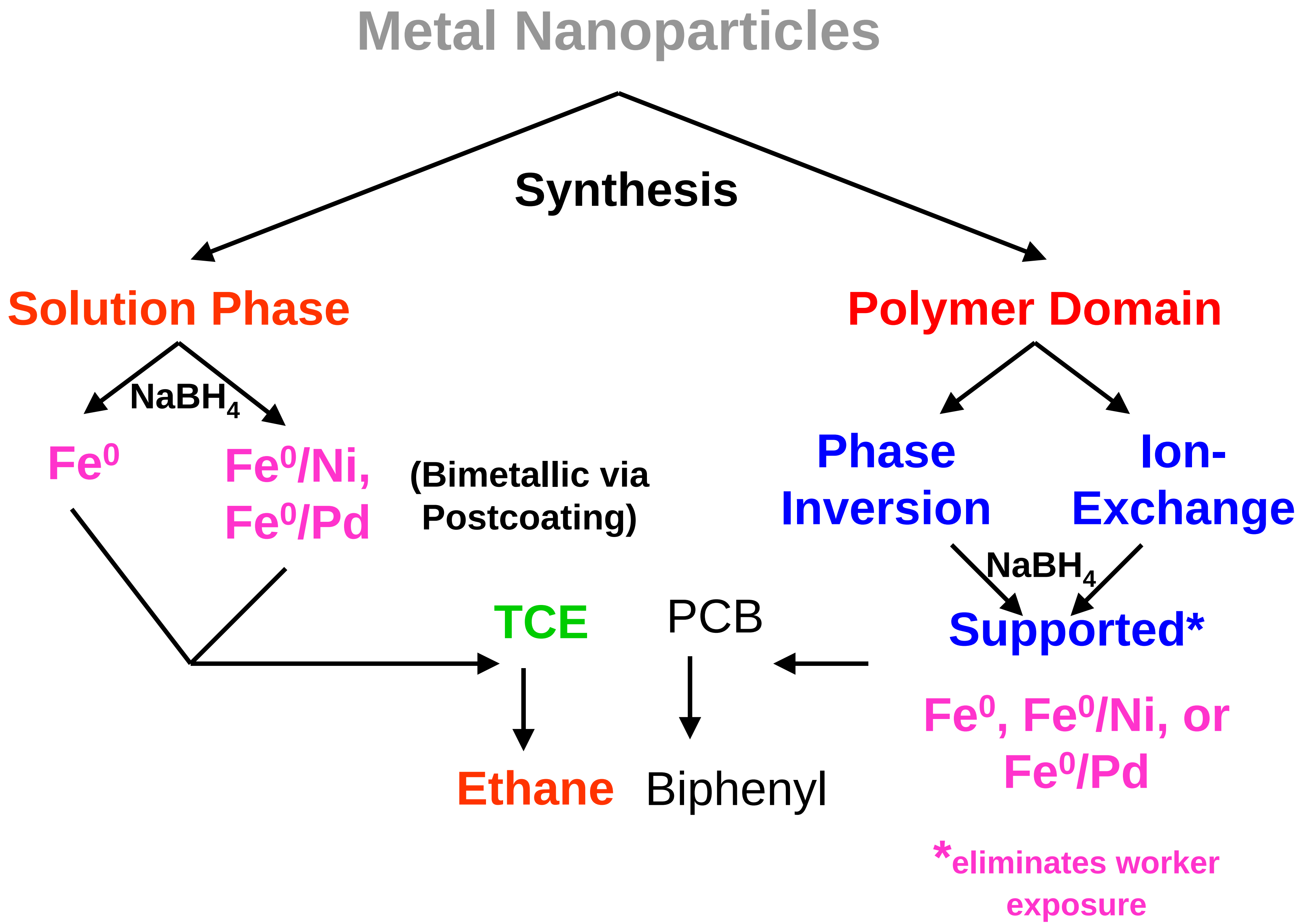
Systems : Chelate Modified **Fenton Reaction**

On-site enzymatic H_2O_2 generation

Groundwater Remediation Using Combined Strategies For Reduction and Oxidation

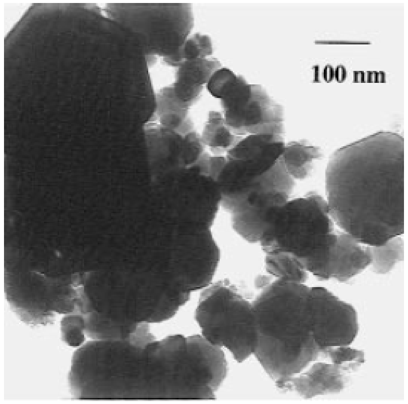


Detoxification of TCE and PCB

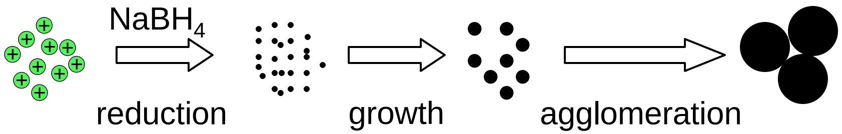


Background (membrane-based nanoparticle synthesis)

Nanoparticle synthesis in aqueous phase

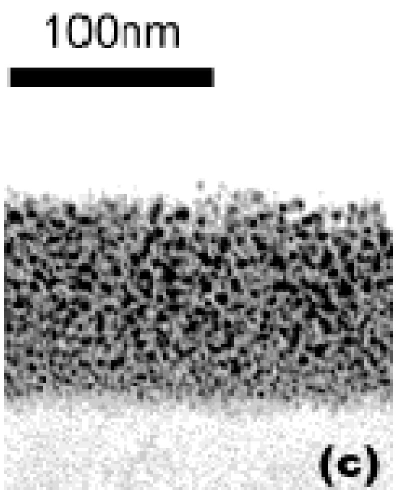


Fe nanoparticles synthesized in solution phase. Wang et al., *Environ. Sci. Technolo.* **1997,** *31,* 2154

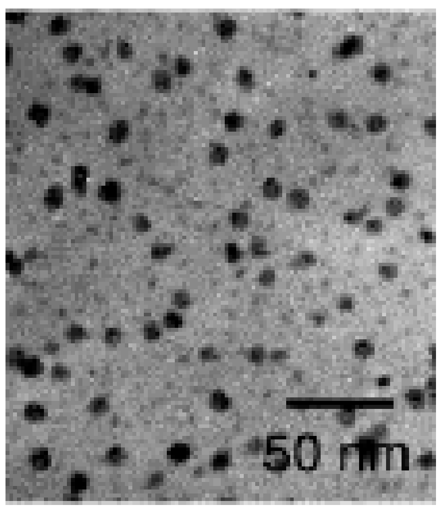


Particle agglomeration and growth in solution without stabilizing agent

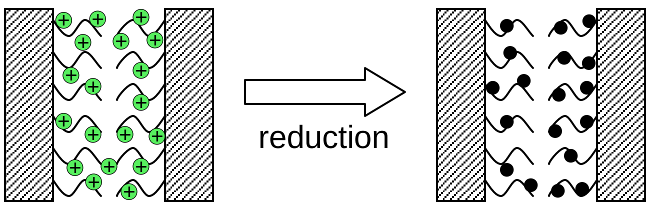
Nanoparticle synthesis in membrane phase



Ag nanoparticles in PAA/PAH multilayer films. Wang et al., *Langmuir* **2002,** *18,* 3370

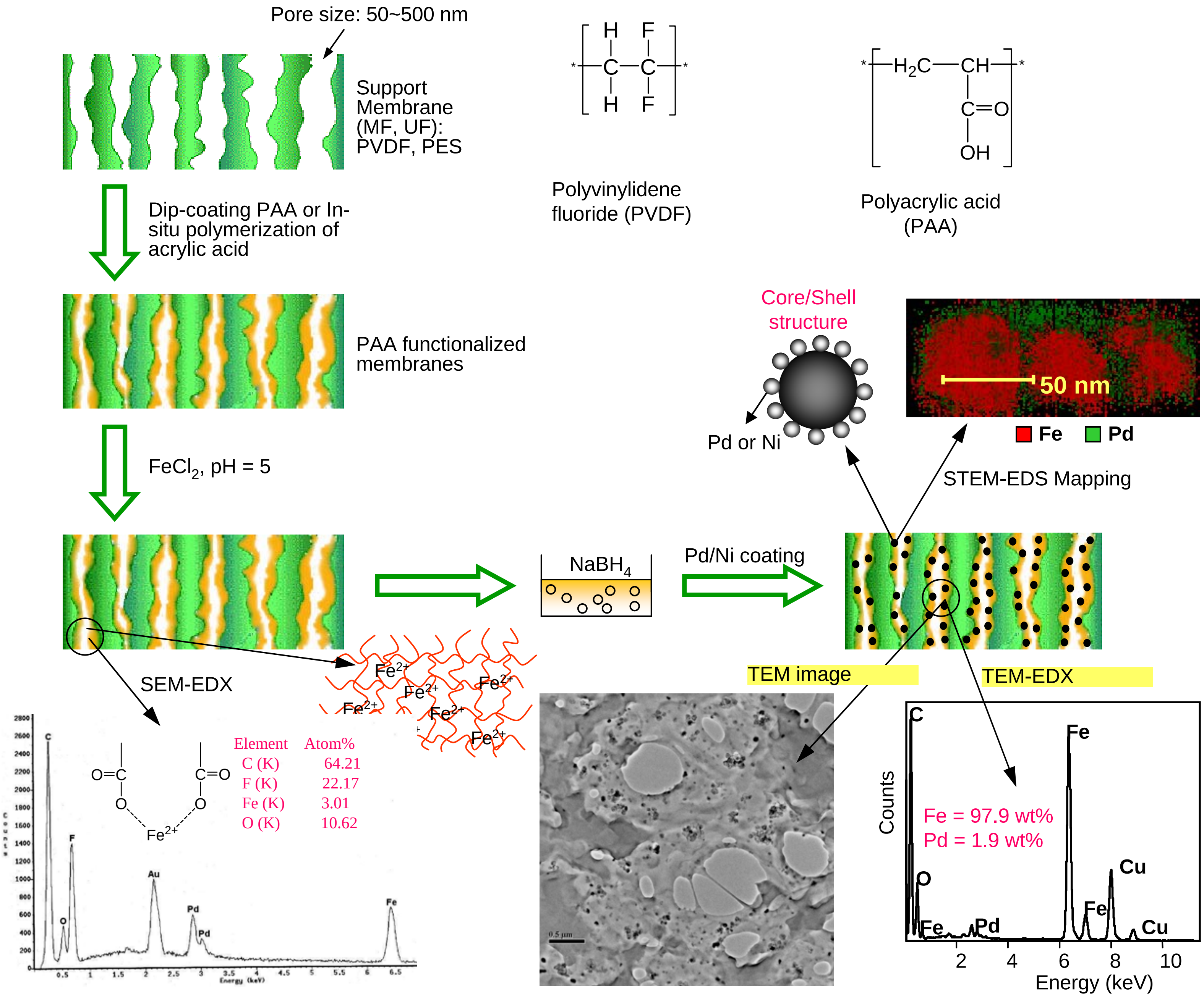


Cu nanoparticles in COOH functionalized polyimide film. Thermal process with H_2 Ikeda et al., *J. Phys. Chem. B* **2004**, *108,* 15599

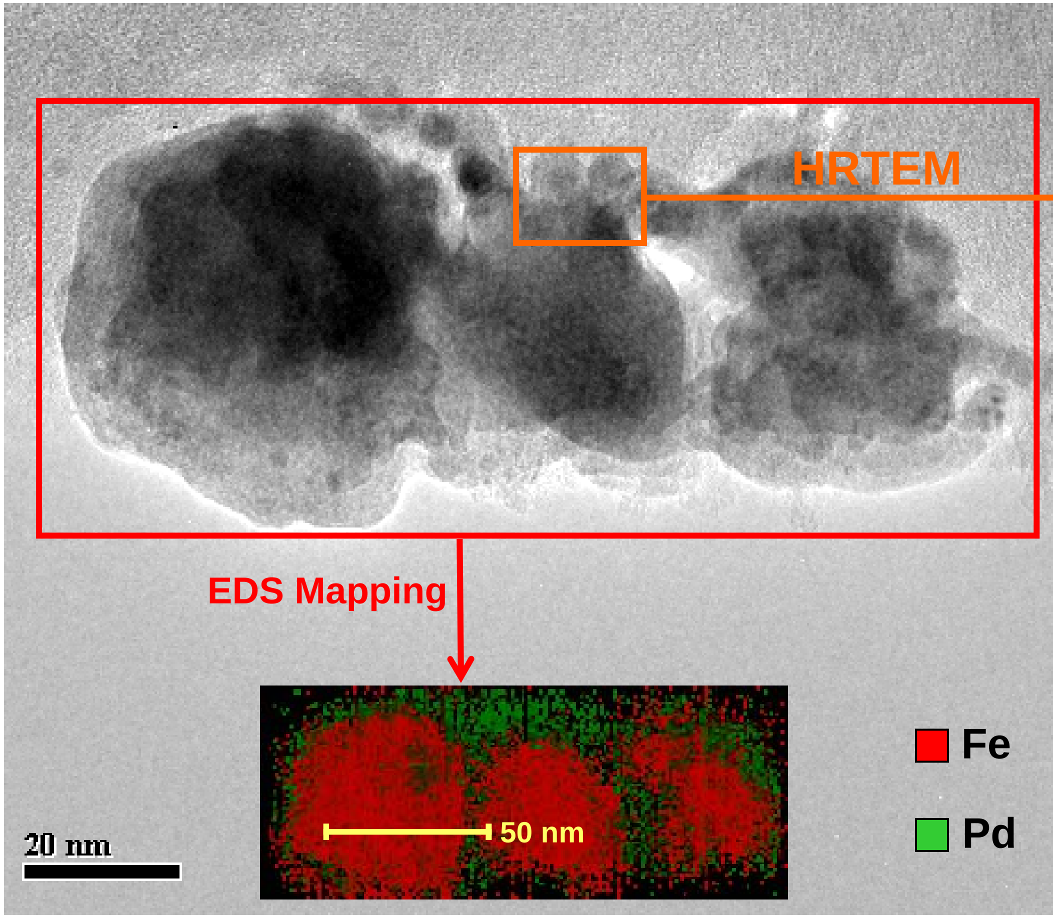


- Prevent particles agglomeration by polymer network
- Control particle size and assembly
- Convective flow
- Recapture of dissolved metal ions

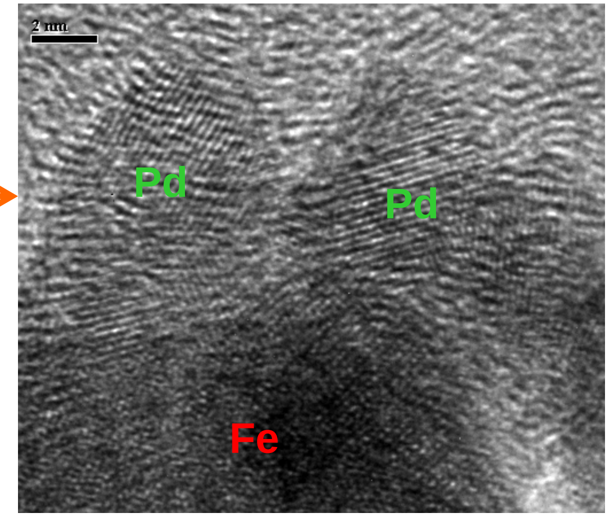
Synthesis of Nanostructured Metals in Functionalized Polymers for Detoxification of Chlorinated Organics

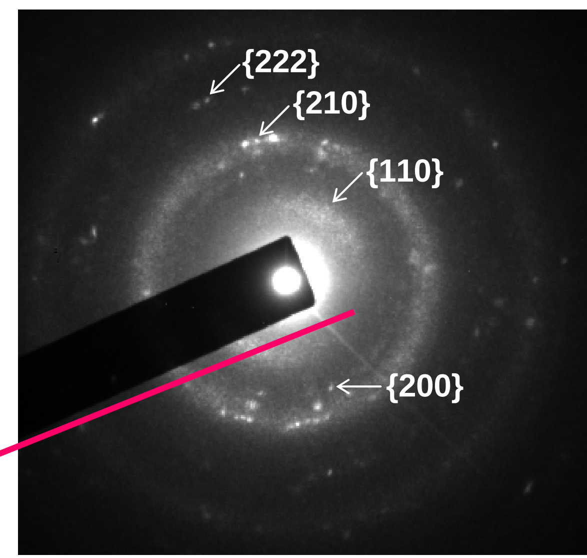


Fe/Pd Nanoparticles Characterization



Fe/Pd (Pd = 2.3 wt%) nanoparticles



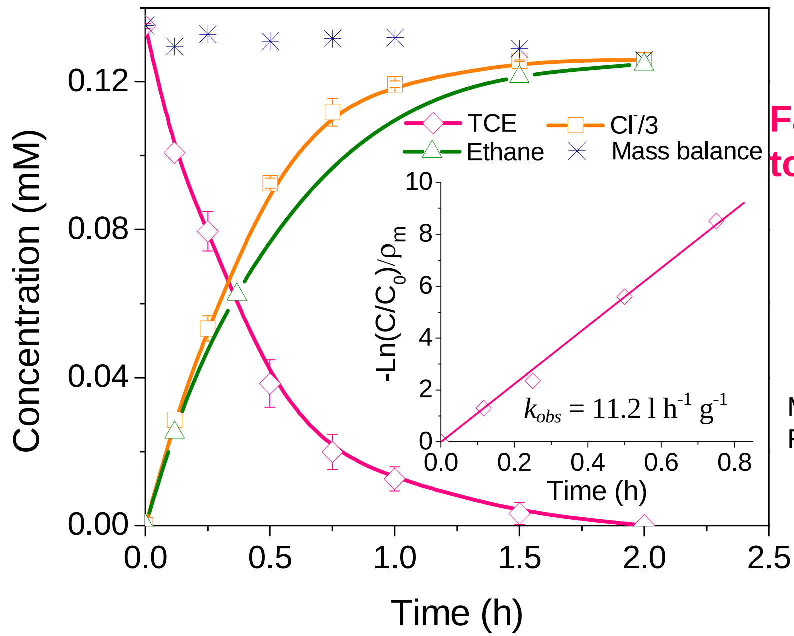


Body center cubic (BCC) crystal structure of Fe^0

Electron diffraction pattern

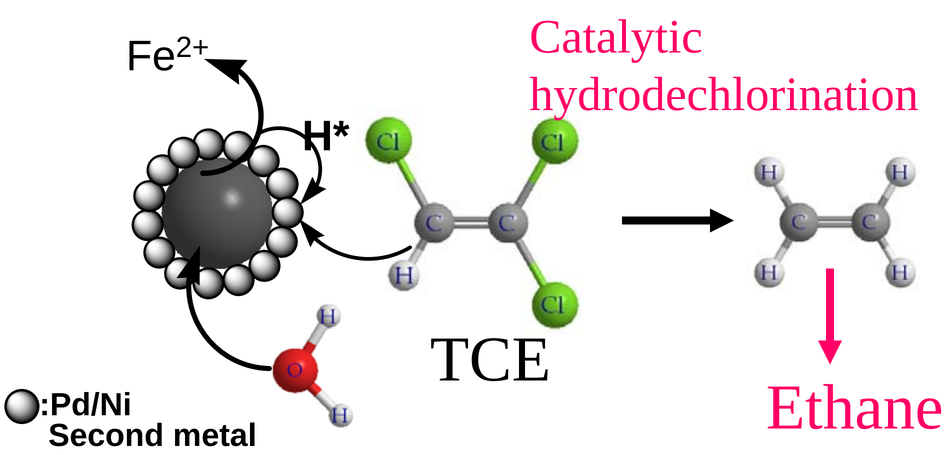
(Suslick, Fang, Hyeon, J. Am. Chem. Soc. 118, 11960-11961, 1996)

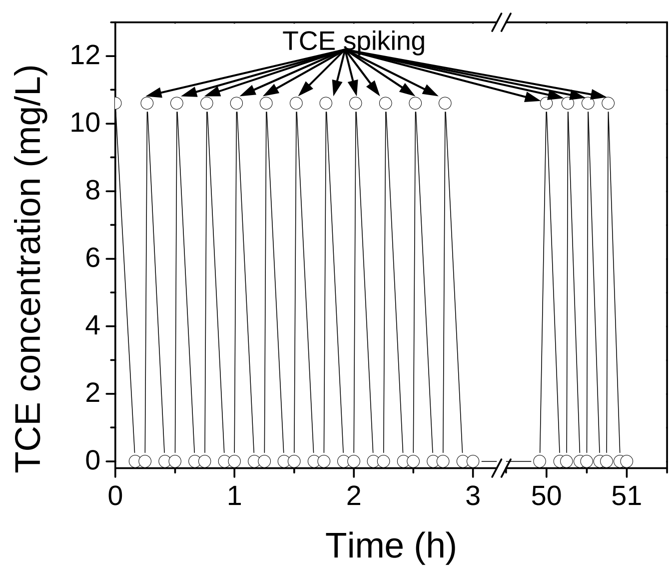
TCE Dechlorination by Nanoparticles



Fast and complete degradation to ethane, no toxic intermediates

Metal loading:4.5mg/20mL
Fe/Ni (Ni = 25 wt%)

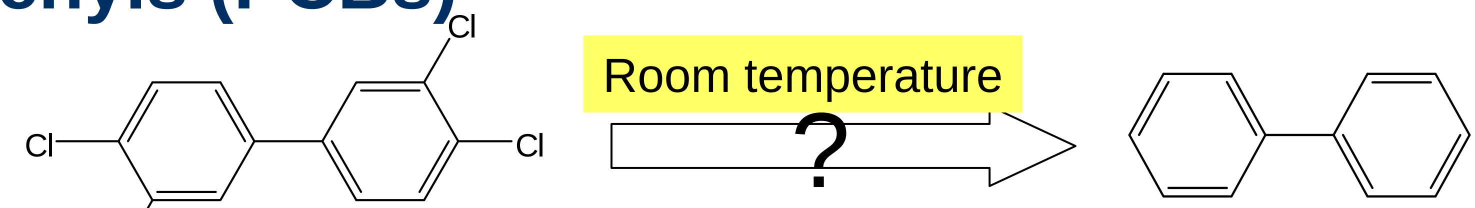




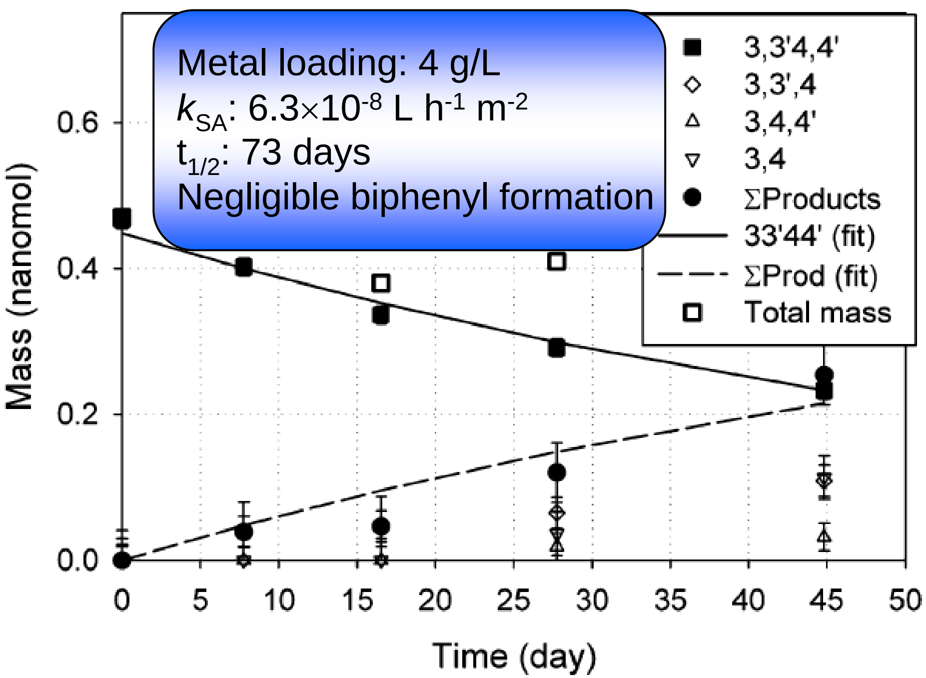
- Fe/Ni (Ni =25 wt%) in PAA/PVDF membranes
- Metal loading: 0.08g/20ml
- 16 cycles of TCE dechlorination

Longevity of Nanoparticle Reactivity

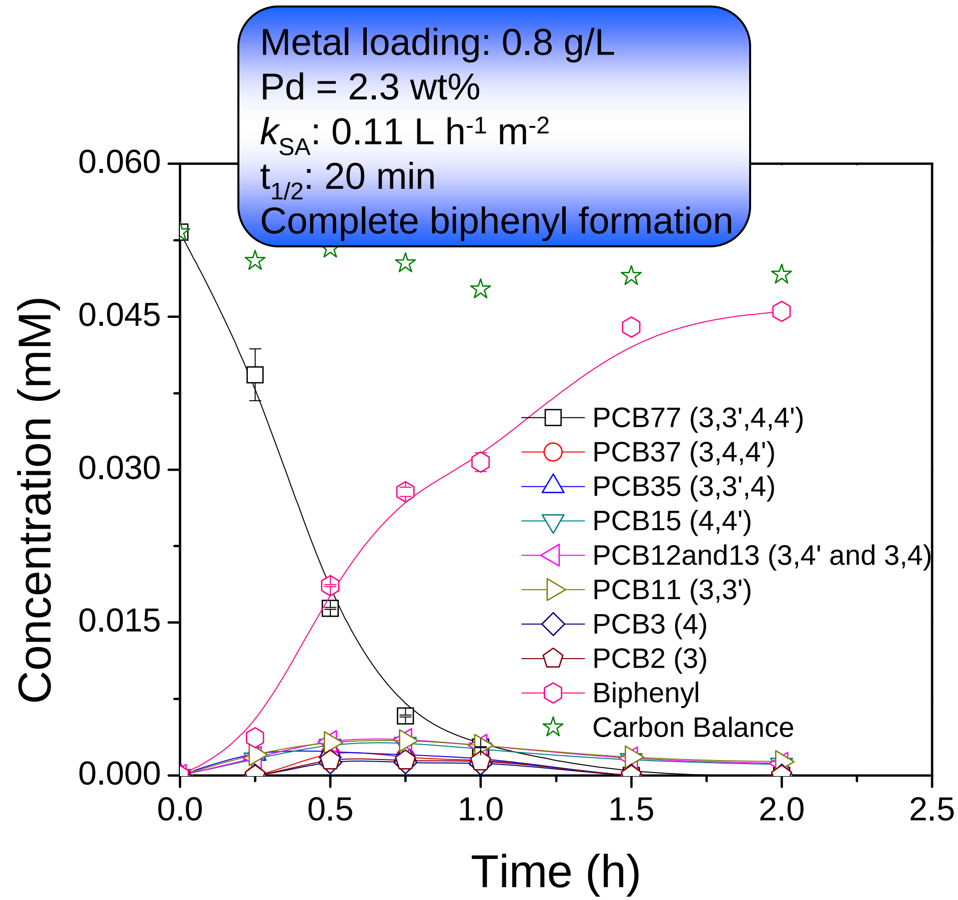
Dechlorination of Polychlorinated Biphenyls (PCBs)



PCB 77 (3,3’,4,4’)



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



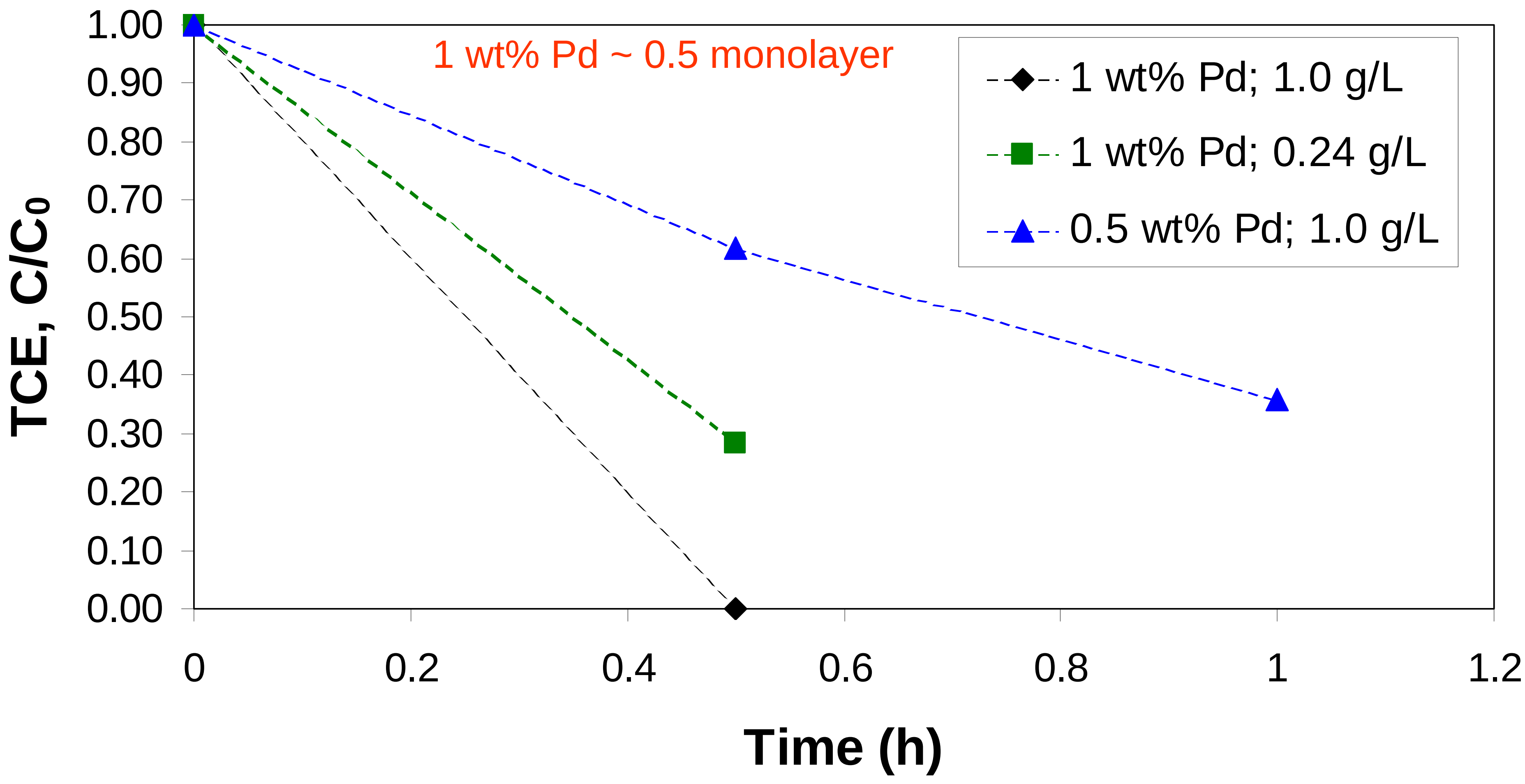
PCB 77 (3,3’,4,4’) dechlorination by membrane based Fe/Pd (Pd=2.3 wt%) nanoparticles at room temperature

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

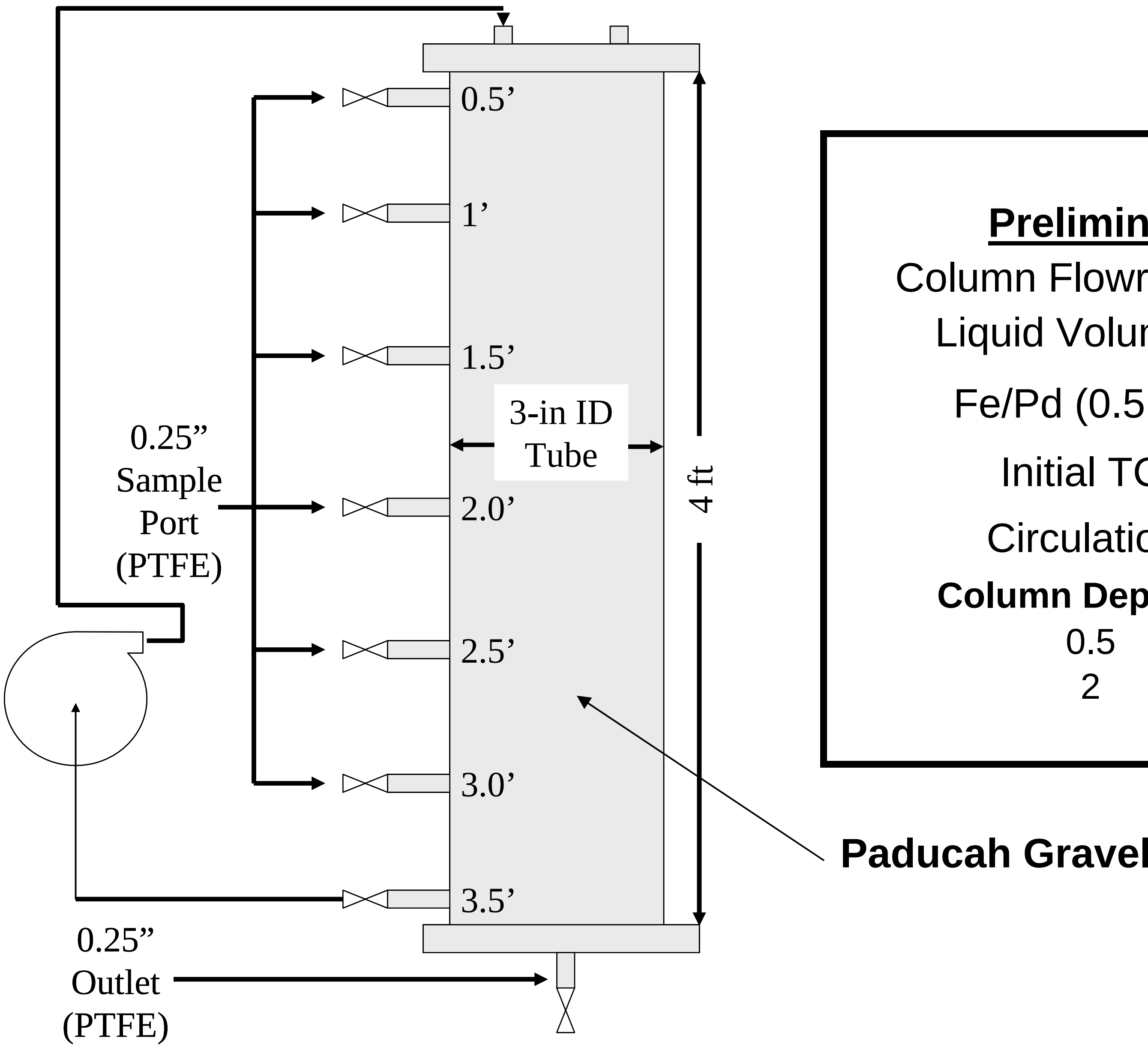
- What **composition** and **metal loading** are necessary for rapid and efficient TCE dechlorination? (**batch** data)
- Will the **presence of non-chlorinated chemical species** present in **Paducah groundwater and soil** alter the performance of Fe-based nanoparticle dechlorination systems? (**batch** 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 in Deoxygenated Paducah Water Using Fe/Pd Nanoparticles with Variable Metal Conditions:

C_0 = 20.5 mg/L; pH = 5



Packed Column Studies for Simulated Groundwater Injection



<u>Preliminary Results</u>

Column Flowrate = 260 ft/day

Liquid Volume = 2.25 L

Fe/Pd (0.5 wt%) = 0.4 g/L

Initial TCE = 46 ppm

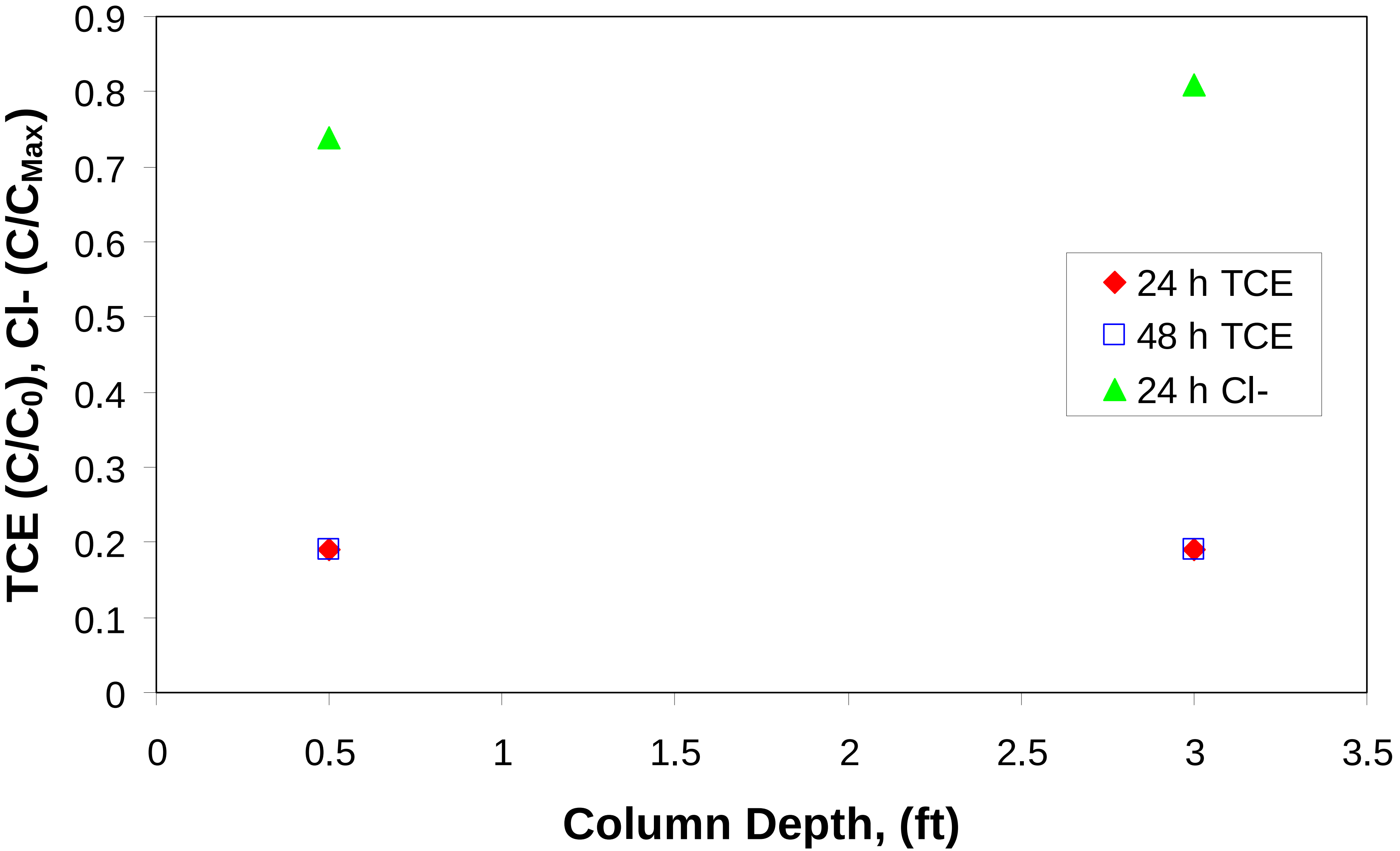
Circulation Time = 4 h

Column Depth (ft)	C/Co
0.5	0.185
2	0.080

Packed Column Studies:

Flowrate = 82 ft/day; Metal Loading = **0.46 g/L** Fe/Pd (0.5 wt%);

C_0 = 25 ppm TCE; pH =7.0



Examination of Material Usuage for the Reduction of 400 ppb TCE Using Fe/Pd Nanoparticles

Time Basis	24	**h**	k_{SA}	1.30E-01	**L.m^{-2}.h^{-1} (Fe + 0.5 wt% Pd)**		
Treatment Diameter	400	**ft**	**Fe/Pd loading**	0.25	**g/L**		
Treatment Depth	20	**ft**	**mass Fe/Pd**	9,433	**g/h =**	20.753	**lbs/h**
Asssumed Porosity	0.4		**Surface Area**	30	**m^2 metal/g**		
Treatment Area	125,664	**ft^2**	**Loading**	7.5	**m^2 metal/L**		
Treatment Volume	2,513,274	**ft^3**					
Treatment C.S. Area	3,200	**ft^2**	**TCE**	400	**ppb**		
Groundwater Velocity	10	**ft/day**					
	0.42	**ft/hr**	**C_{TCE} @ 1h**	0.000	**ppb**		
Volume per hour	1,333	**ft^3/h**	**TCE reacted**	1.15E-01	**moles/h**		
	37,733	**L/h**					

Fe:TCE ratio	4:1	
moles Fe consumed	4.59E-01	
mass Fe consumed	25.66	**g/h**
	0.056	**lbs/h**
Fe remaining	9,407.67	**g/h**
	20.697	**lbs/h unused**

Note: one can treat 38000 liters of water with 26 g of nano Fe particles

Detoxification by Chelate-Based Modified Fenton Reaction

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

*Superoxide Radical Formation: $OH\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet$ $HO_2\bullet \rightarrow H^+ + O_2\bullet^-$

Required Materials for Chelate-Based Modified Fenton Reaction

Citrate

http://www.hort.purdue.edu/ext/senior/fruits/orange1.htm

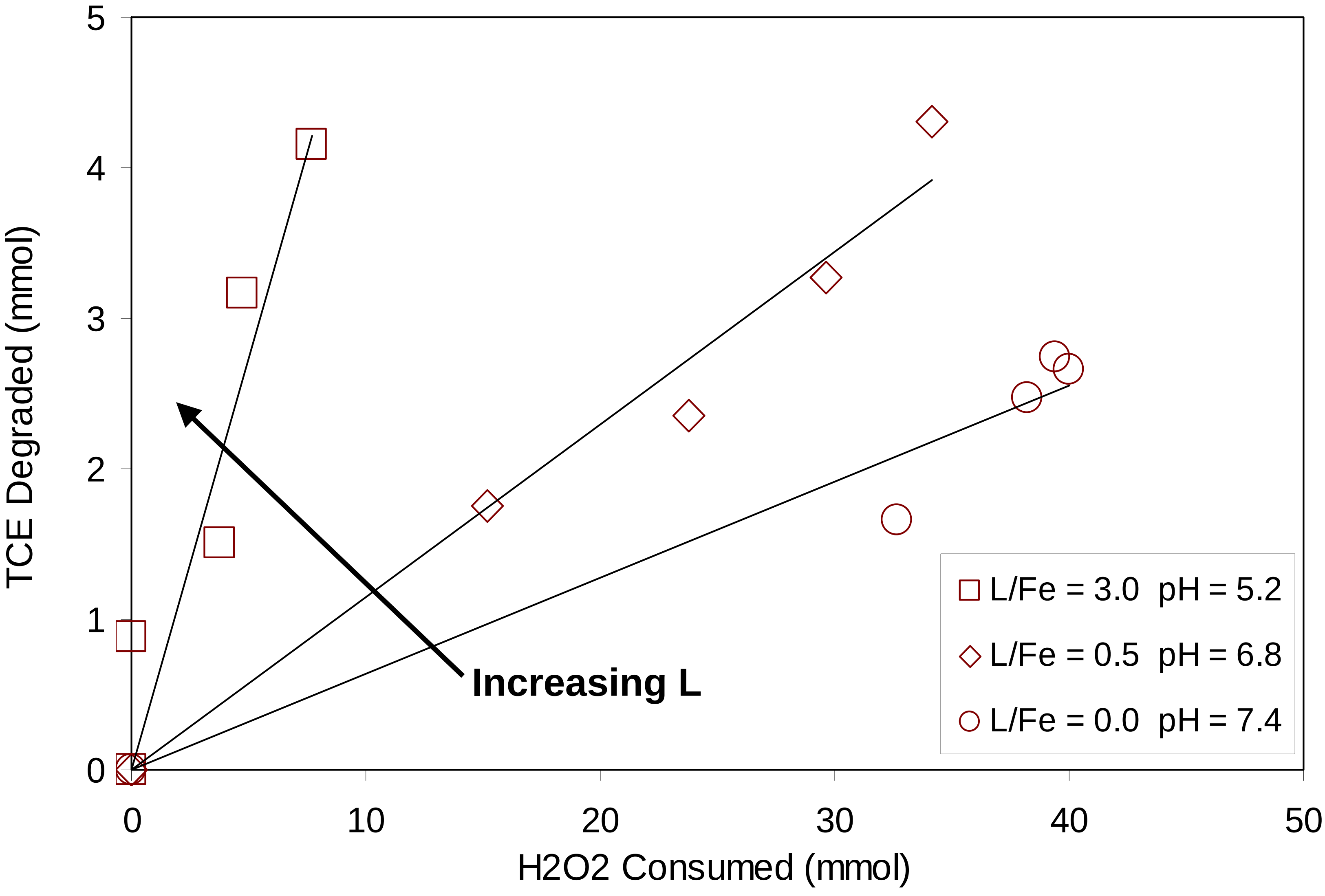
Ferrous Sulfate

http://www.drugstore.com/popups/largerphoto/default.asp?pid=77653&catid=39521&size=300&trx=29888&trxp1=77653&trxp2=1

Hydrogen Peroxide

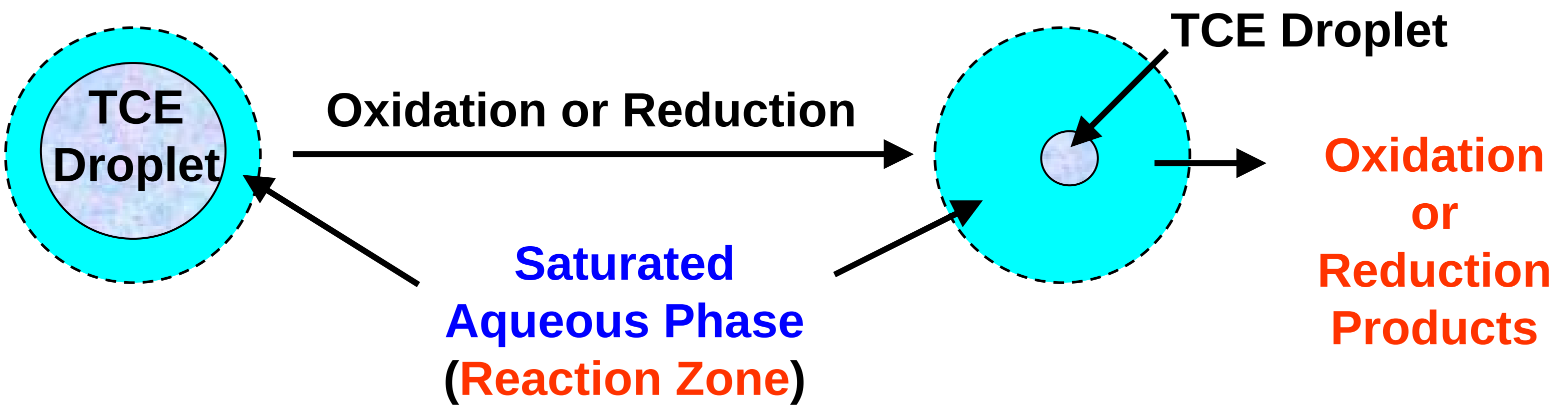
http://pics.drugstore.com/prodimg/73864/200.jpg

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

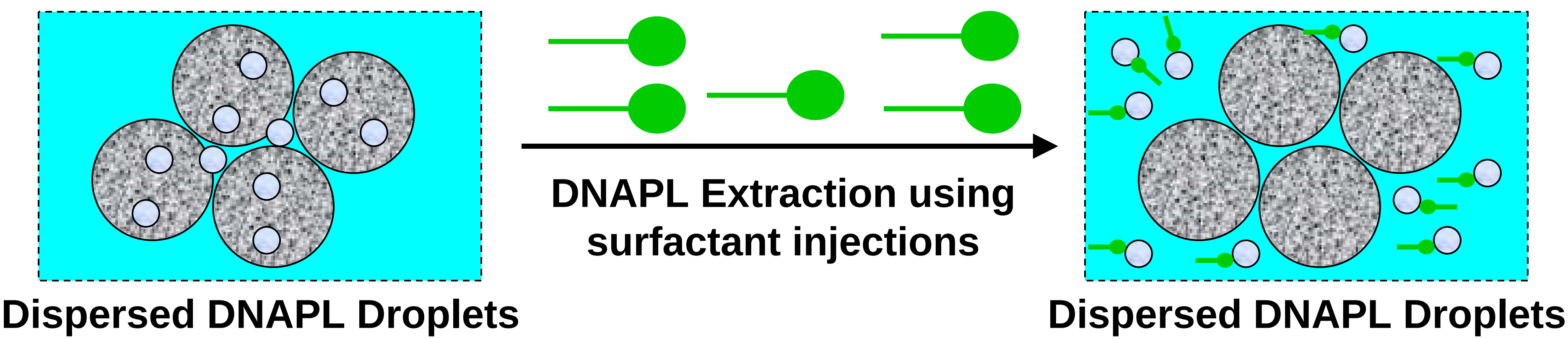


The Challenges of DNAPL

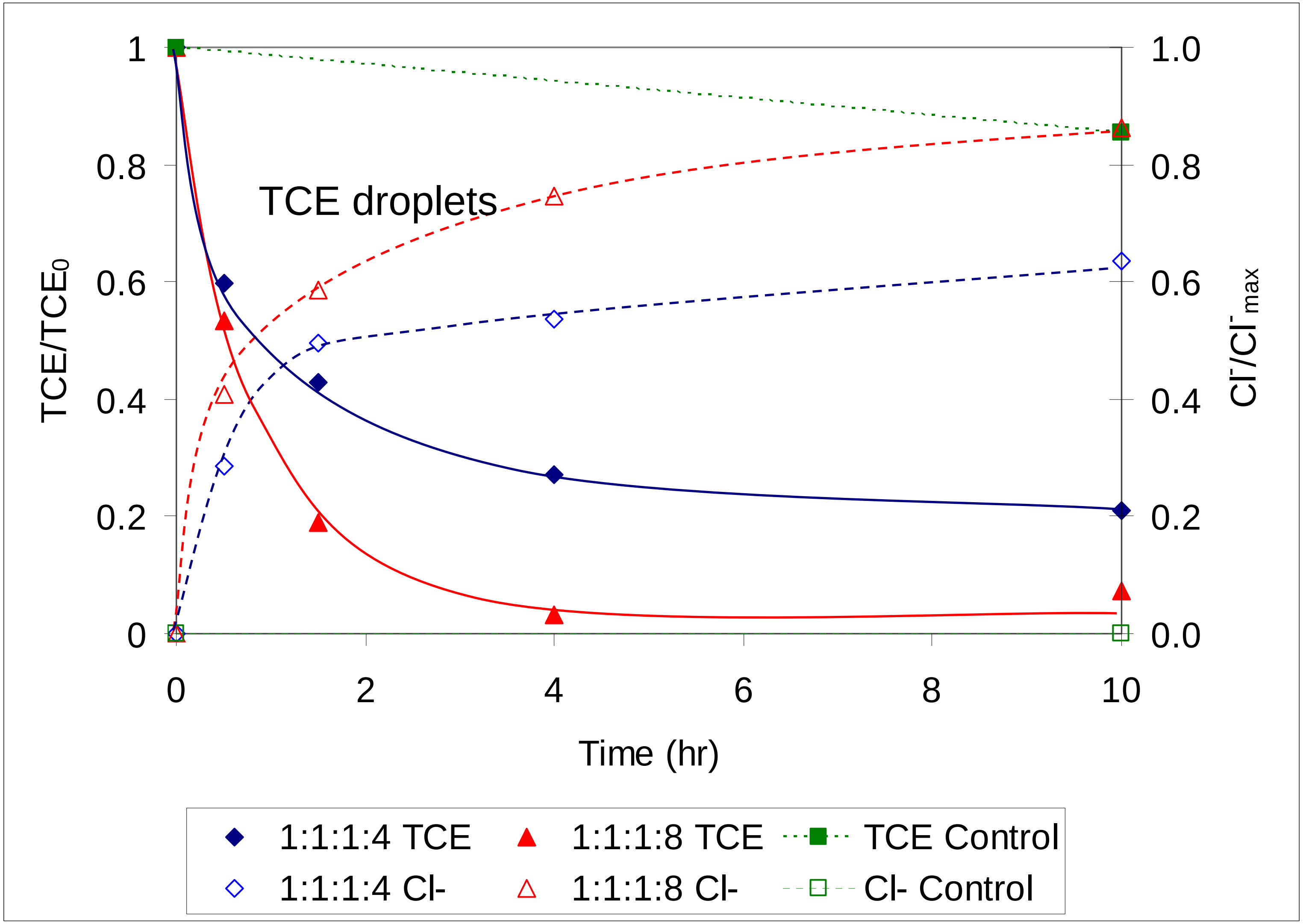
1.) TCE droplets dispersed in the aqueous phase will act as a source of TCE and shrink as mass is lost to the aqueous phase. The mass transfer between phases may have substantial impact on the observed reaction time for both oxidation and reduction.



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 (initial pH=7.0, no further adjustments made) Using DIUF Water with DNAPL (2000ppm TCE) and Varying Fe(II):H_2O_2 Molar Ratio



Acknowledgements

- NIEHS-SBRP Program
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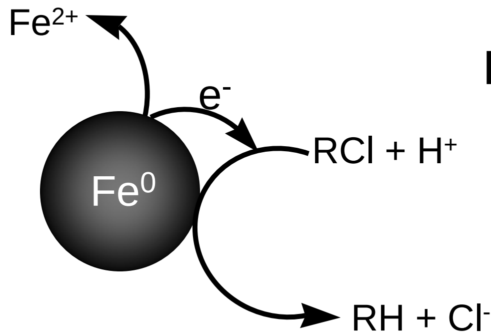
- UK Environmental Research and Training Laboratory (ERTL) (John May & Tricia Coakley)
- UK Electron Microscopy Facility (Dr. Alan Dozier)

Extra slides

Background (reductive dechlorination at room temperature)

Single Fe^0 system



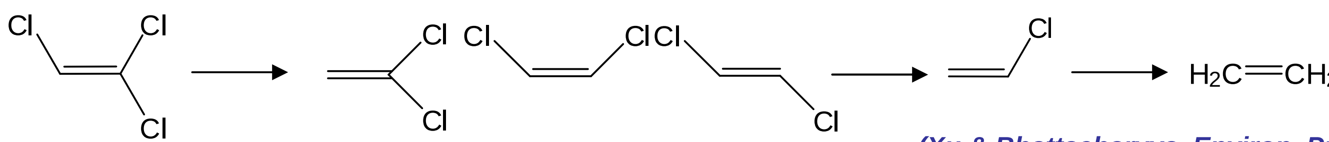
Reaction mechanism: electron transfer

$$Fe^0 \rightarrow Fe^{2+} + 2e^-$$

$$RCl + 2e^- + H^+ \rightarrow RH + Cl^-$$

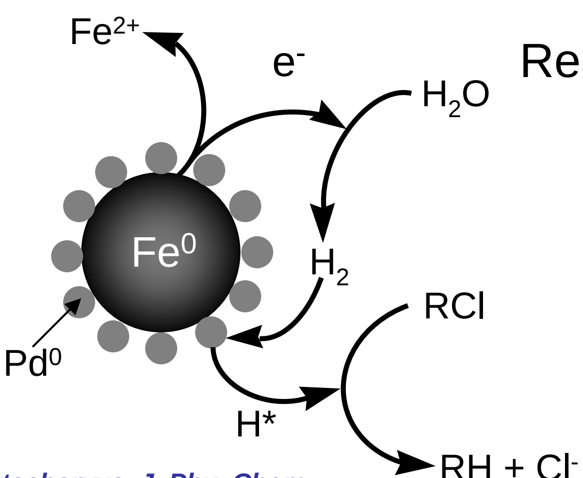
$$RCl + Fe^0 + H^+ \rightarrow Fe^{2+} + RH + Cl^-$$

(Matheson et al., Environ. Sci. Technol. 28, 2045-2053, 1994)



(Xu & Bhattacharyya, Environ. Prog., 24, 358, 2005)

Bimetallic system

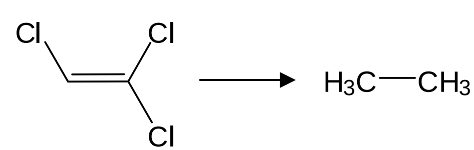


Reaction mechanism: catalytic hydrodechlorination

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$$

$$H_2 + Pd \rightarrow Pd\text{-}H + H^*$$

$$RCl + H^* \rightarrow RH + Cl^-$$



(Meyer and Bhattacharyya, J. Phy. Chem, 2007;Xu et al, J.Nanopar.Res. 7, 449-467, 2005)

Technology Enhancement: On-site Generation of Chelate and H_2O_2

HYPOTHESIS

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

MOTIVATION

On-Site source of peroxide and chelate will eliminate the need for concentrated chemical Storage by using simple Glucose as a substrate