Green and Responsive Materials for Remediation

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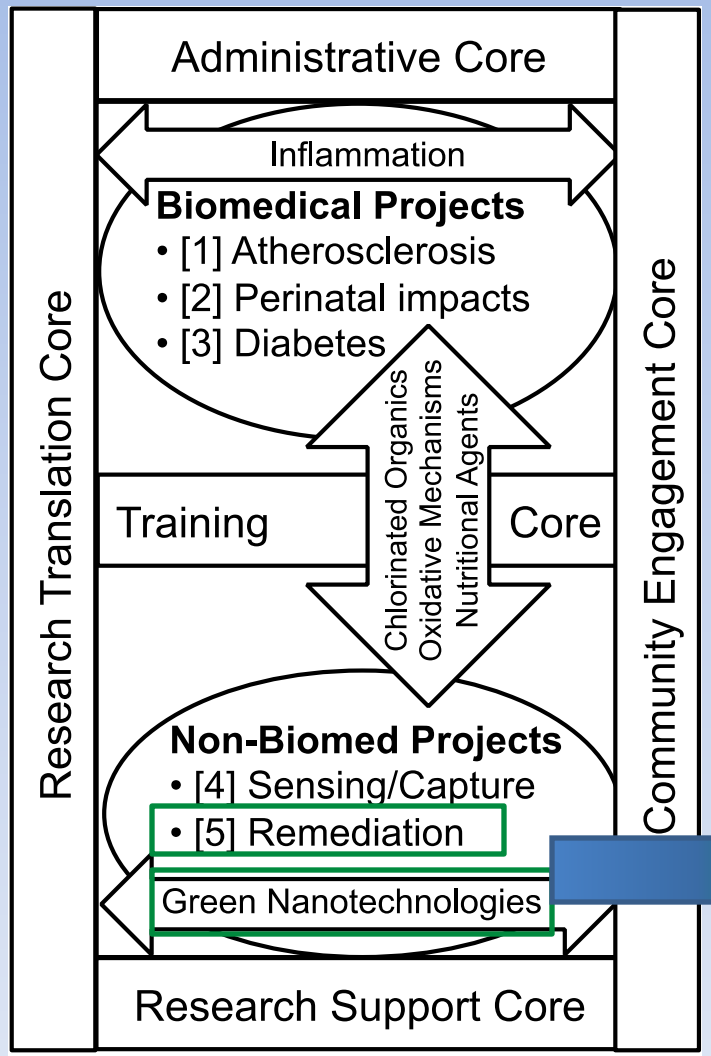
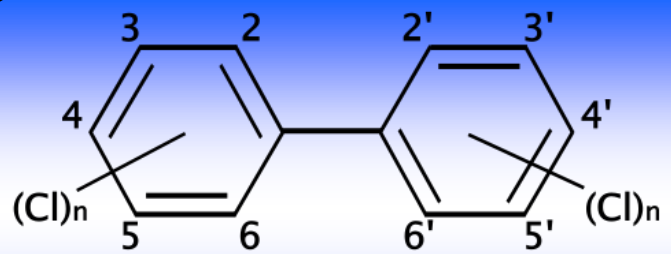
NIEHS-SRP Annual Conference
Raleigh, NC, 2012

University of Kentucky Superfund Research Center (UK-SRP)



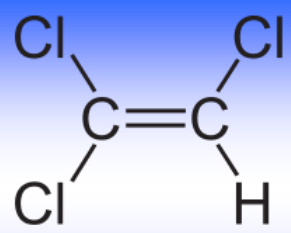
Green and Responsive Materials for Superfund Chemicals Degradation

Chlorinated Organics Contamination



Polychlorinated biphenyls (PCBs)

Solubility in water: less than **5.9 mg/L**

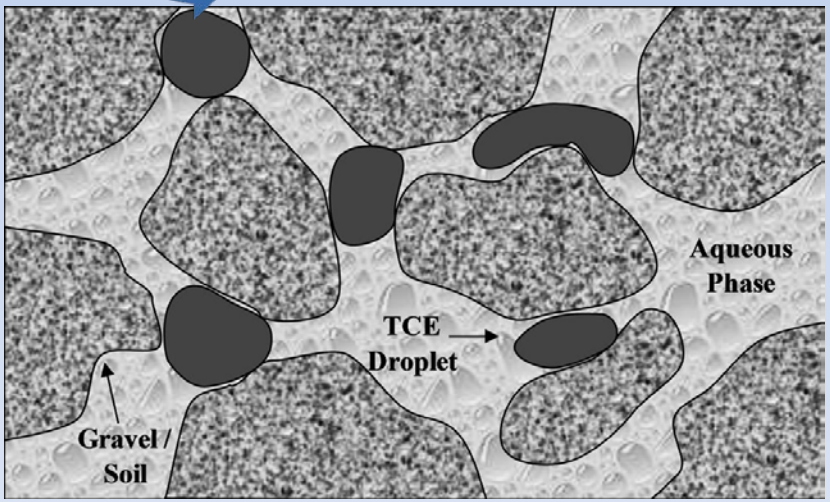


Trichloroethylene (TCE)

Solubility in water: **1280 mg/L**

The water solubility of a PCB compound decreases as the degree of chlorination increases

Associated with the solid fraction



(adapted from Kennedy and Lennox, 1997)

Widely exist in serious hazardous waste sites in the form of dense nonaqueous phase liquids (DNAPL)

Green Synthesis of Nanoparticles in Membranes

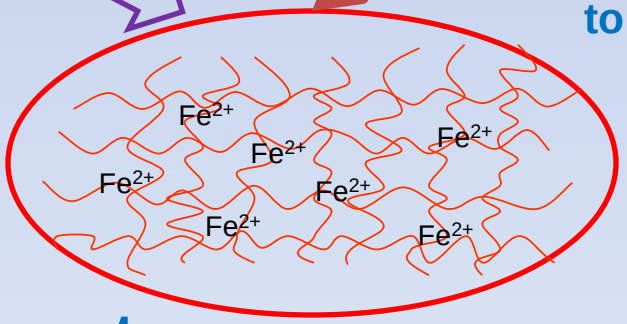
http://bodybyreveal.com/importance-of-antioxidants/

Vitamin C

http://www.drugstore.com/

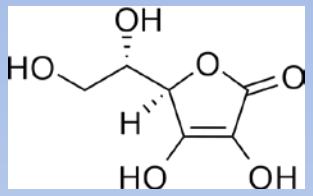
http://berriesandchampagne.com/?cat=11

Tea Extract

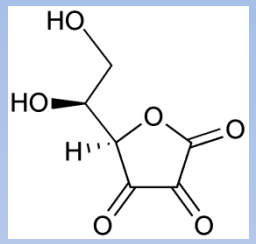


Can We Use the Membrane to immobilize the iron?

Vitamin C (Ascorbic Acid)

2 

ascorbic acid

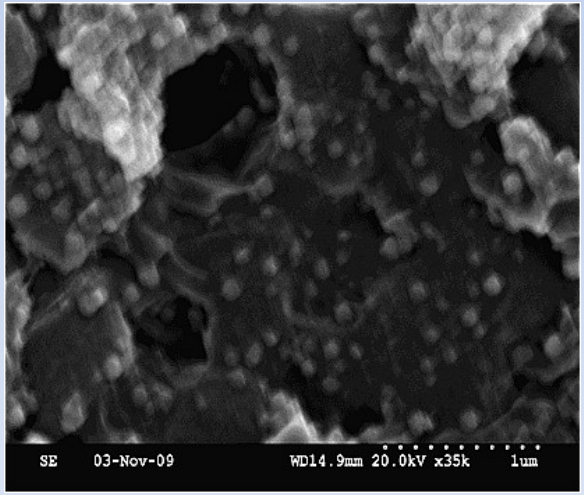
→ 2 

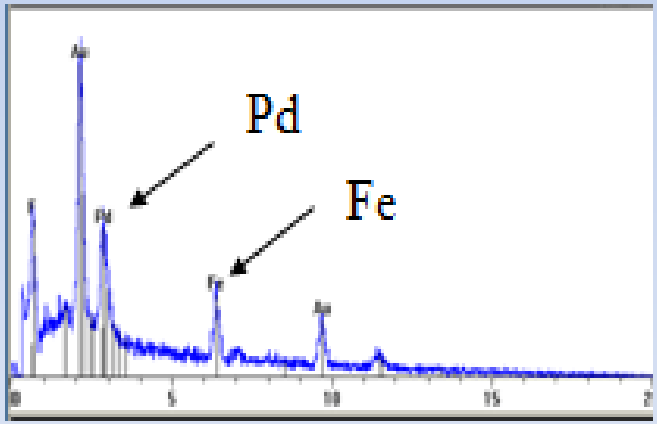
dehydroxyascorbic acid

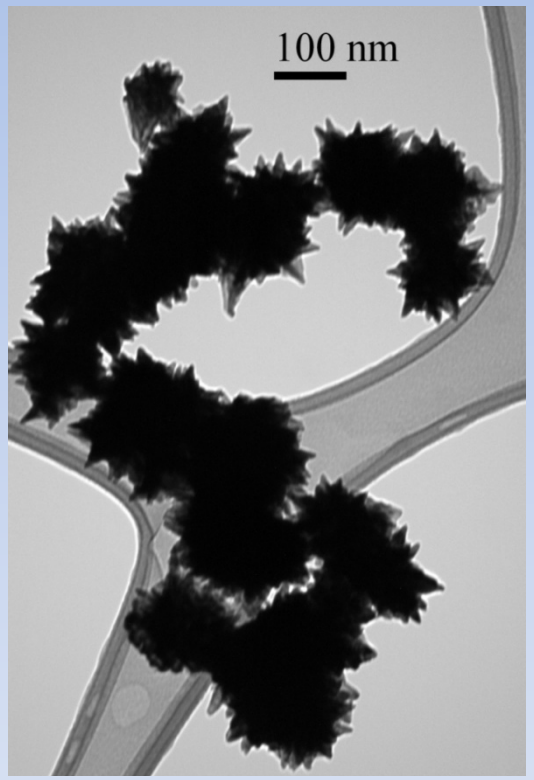
+ 4*e*- + $4H^+$ E^0 = -0.116 V

$2/3\ Fe^{3+} + 2e^- \longrightarrow 2/3\ Fe$ E^0 = -0.0247 V

$Pd^{2+} + 2e^- \longrightarrow Pd$ E^0 = 0.951 V

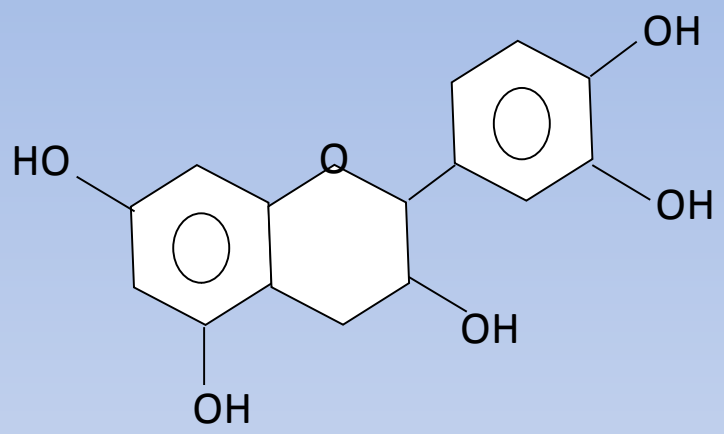




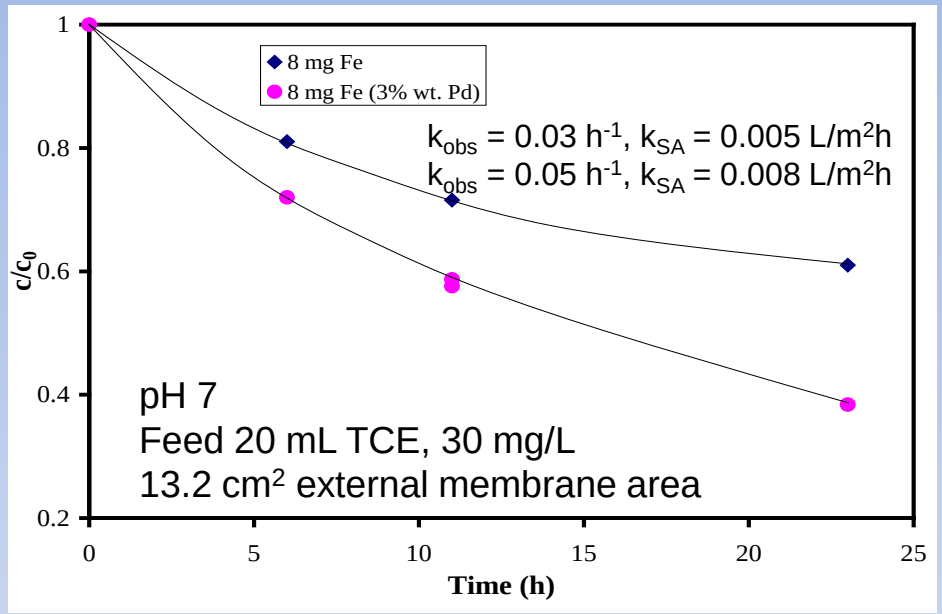


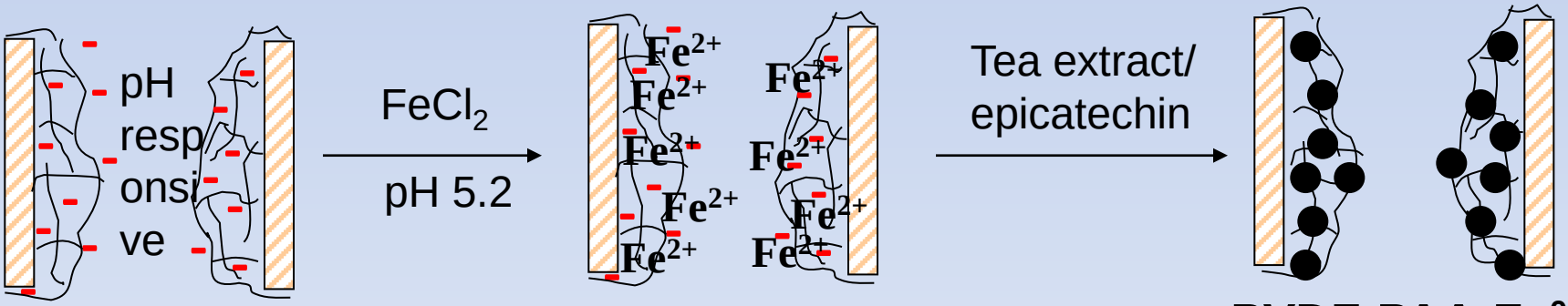
Varma, et al, Crystal Growth & Design, 2007
Liu, Roberts, et al. Langmuir, 2009; quoted from Lewin, 1976

Green Tea Extract



Epicatechin





PVDF-PAA **PVDF-PAA-Fe^{2+}** **PVDF-PAA-Fe^0**

Schematic of Fe nanoparticle synthesis in PAA-coated PVDF membrane (using tea extract as a reducing agent) (Smuleac,Varma, Sikdar, and Bhattacharyya, J. Membrane Sci, 2011, 379: 131-137.)

Technology Enhancement of Remediation

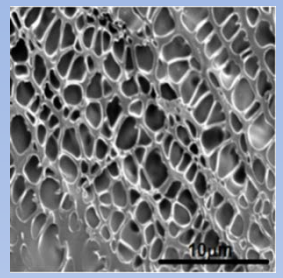
HYPOTHESIS

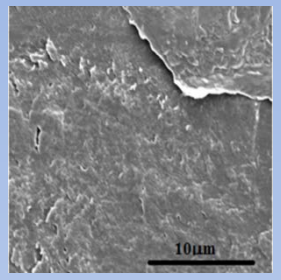
NPs can be synthesized in temperature responsive hydrogels (used in biomedical field) with tunable pollutant partitioning and subsequent increase in PCB, TCE, degradation rates

Transfer knowledge from medical field

MOTIVATION

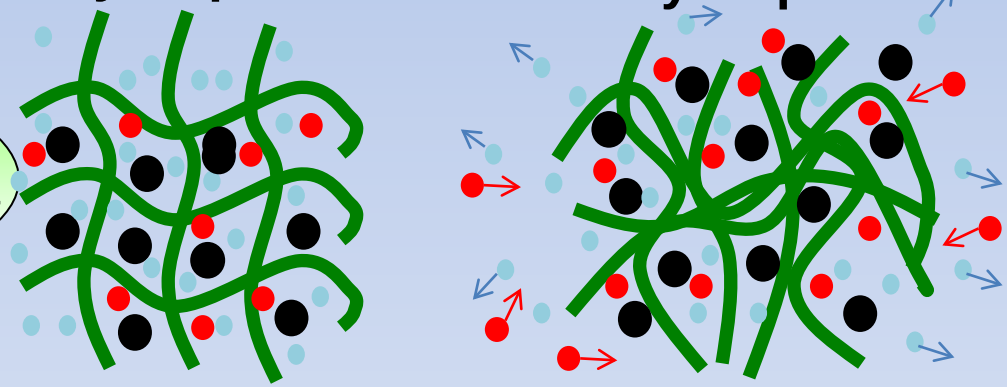
Magnetic nanoparticles encapsulated in temperature responsive hydrogel were used for remote control of drug delivery.





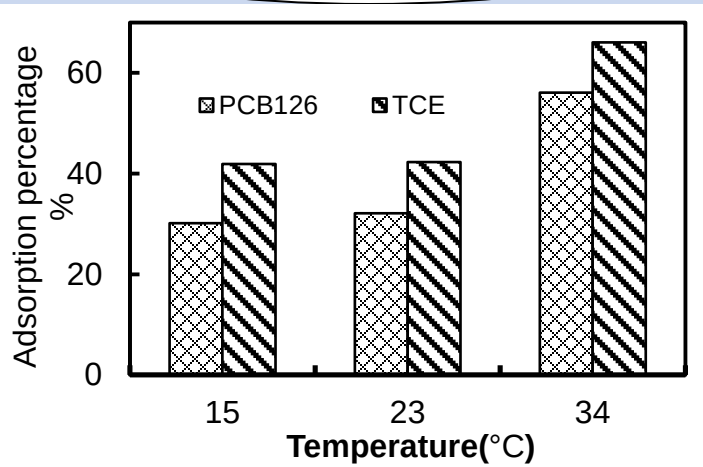
Below LCST → **Above LCST**

Hydrophilic **Hydrophobic**



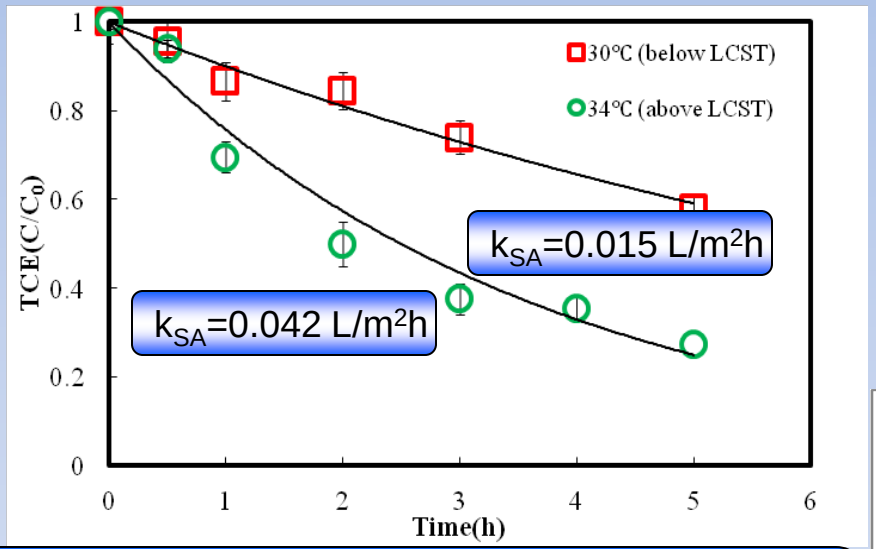
Water **Toxic organics** **metallic NPs**

LCST-lower critical solution temperature

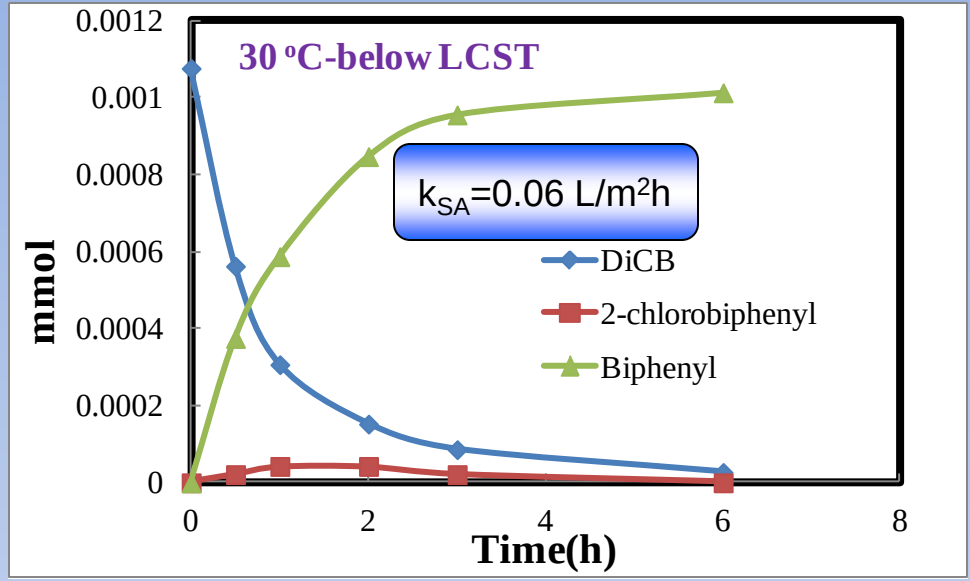


Xiao, L.; Isner, A. B.; Hilt, J. Z.; Bhattacharyya, D.
J. Appl. Polym. Sci. 2012. DOI: 10.1002/app.38335.

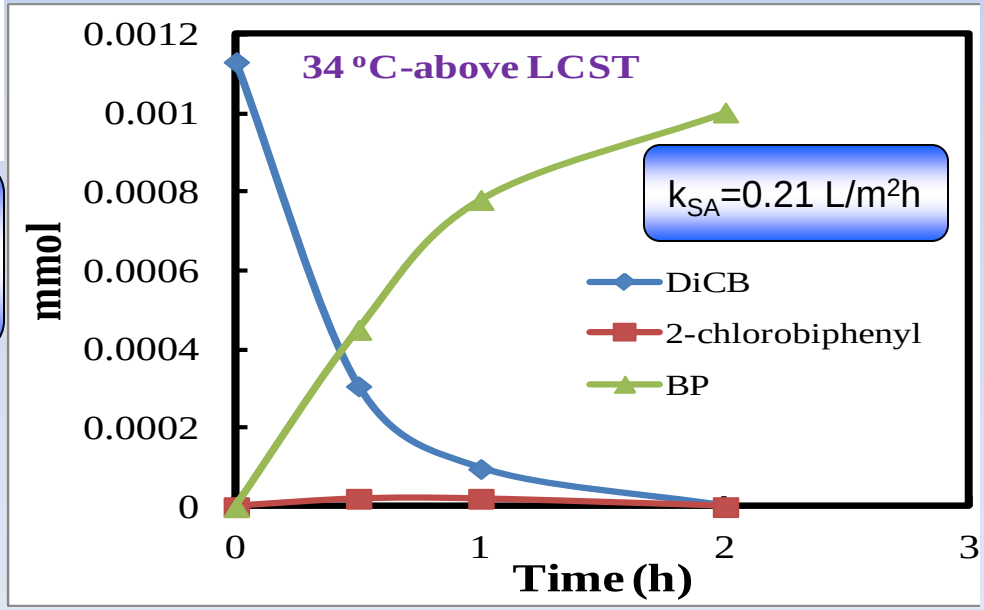
Enhanced Degradation by Temperature-Responsive Hydrogel Immobilized Nanoparticles

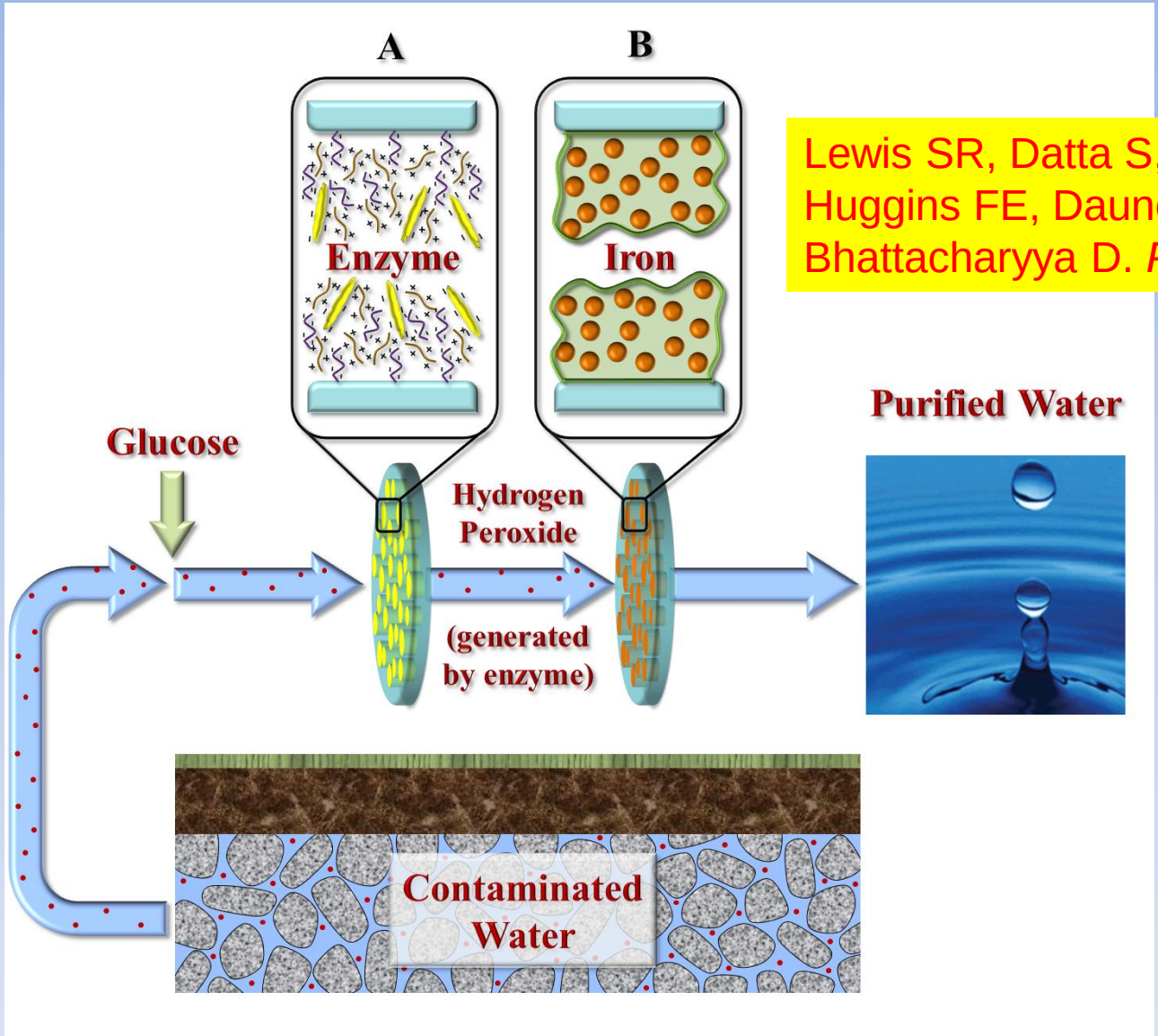


Iron loading : 0.3 g/L; Pd loading: 1.5%; Volume 43 mL; pH 6.5; Initial TCE conc. 30mg/L.



19 mg Fe, 2.4 wt% Pd; Volume: 40 mL,pH: 6.5
Feed conc. DiCB 6 mg/L(0.0011 mmol)

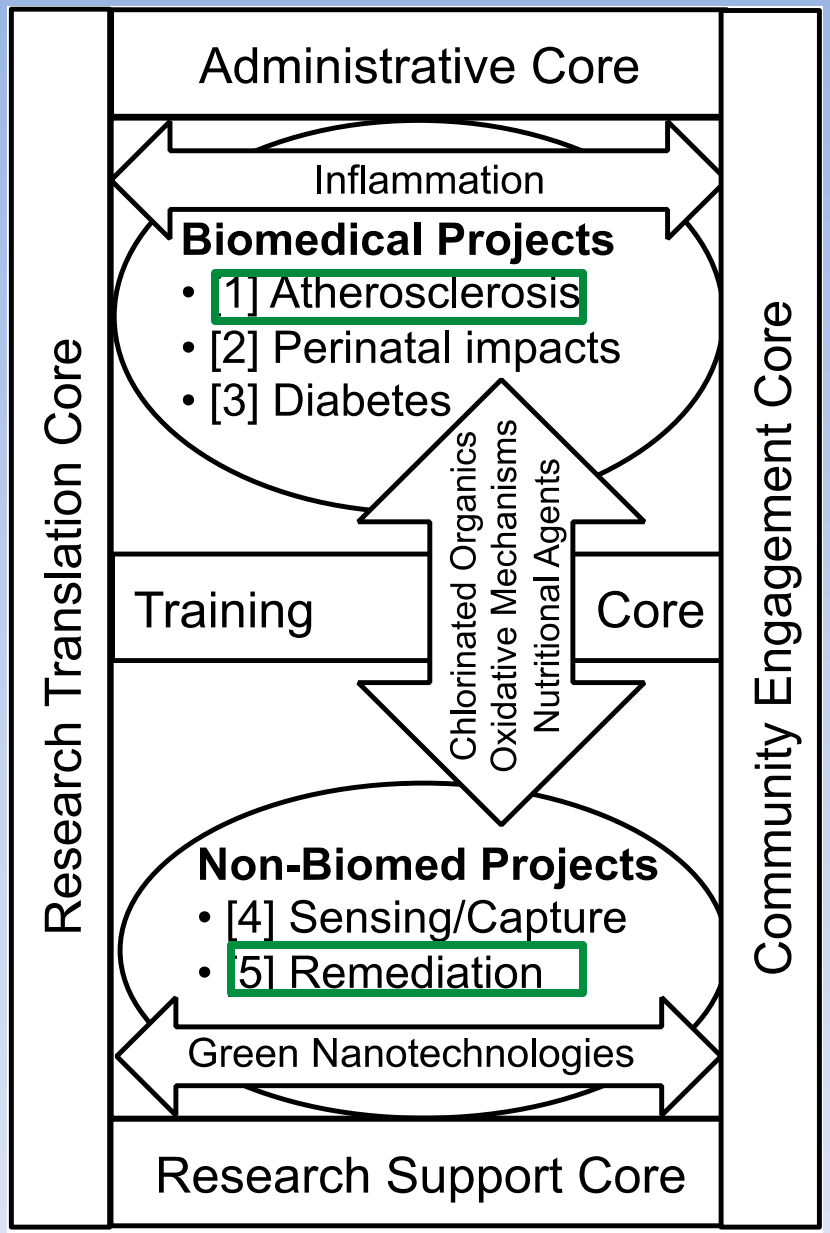




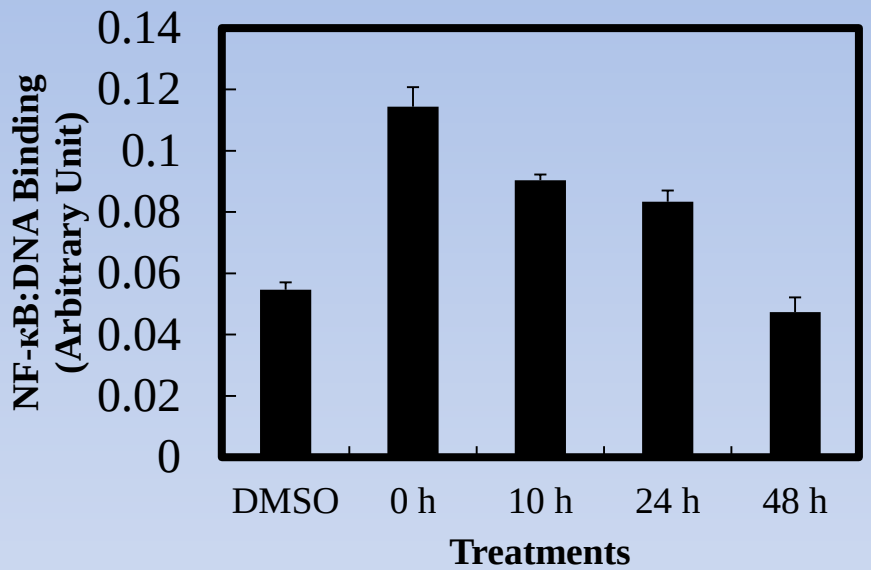
Lewis SR, Datta S, Gui M, Coker EL, Huggins FE, Daunert S, Bachas L, Bhattacharyya D. *PNAS (May 23,2011)*

Stacked-Nanocomposite Membranes for Oxidative Degradation

Modular double-functional membrane platform with immobilized enzyme and iron for clean water production. (A and B: expanded views of nanostructured membrane pores).

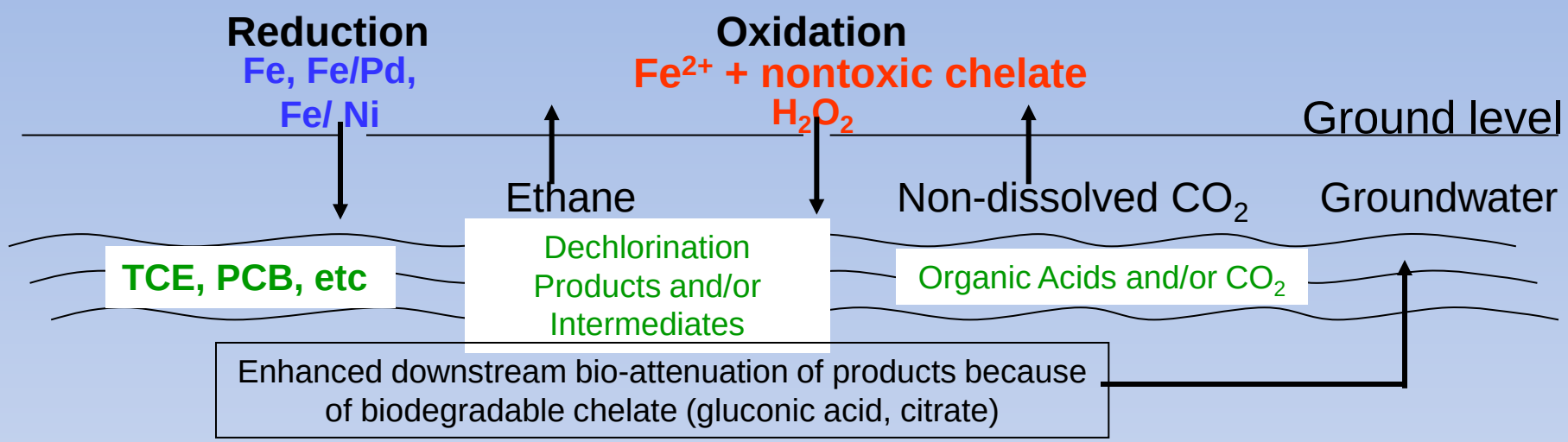


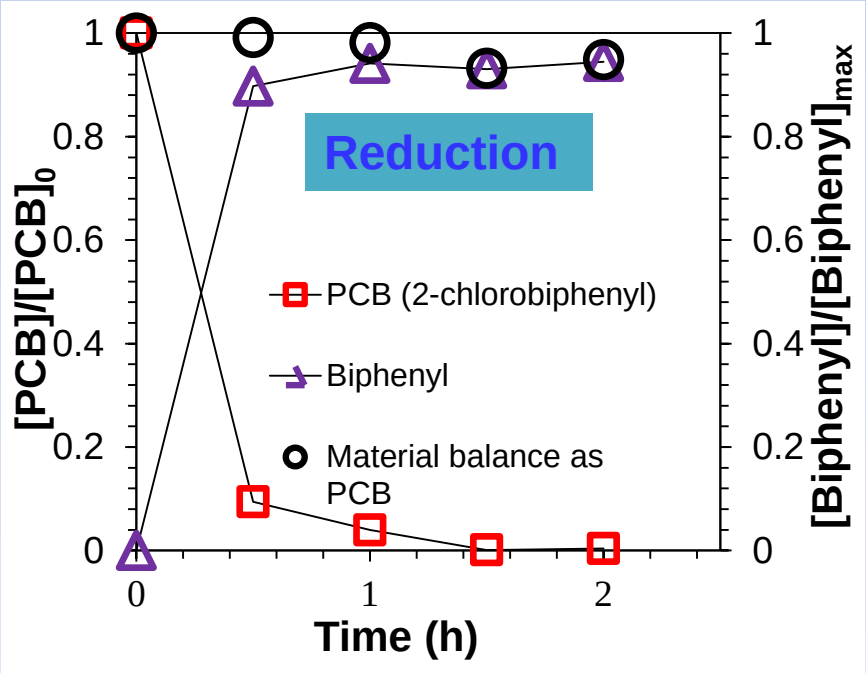
Collaborative study between Projects 1 and 5 to test the hypothesis that dechlorination (remediation) of PCBs reduces their toxicity and pro-inflammatory potential.

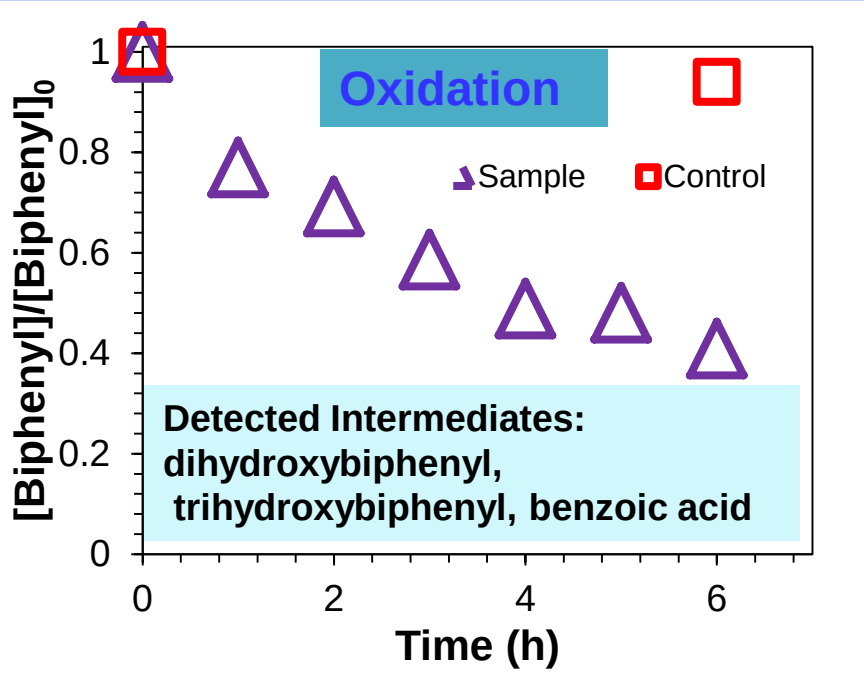


DNA binding of NF-κB, a critical pro-inflammatory transcription factor, is decreased following dechlorination.

Remediation by Combined Strategies For Reduction and Oxidation







Conclusions

Novel platform for both reductive and oxidative dechlorination

- Successfully prepared NPs by Green Synthesis
- Enhanced the degradation of TCE and PCBs
- Significant toxicity reduction by combined reductive and oxidative pathway
- This method has potential for broader green remediation, such as for Triclosan

Acknowledgements

- NIEHS/SRP, and DOE-KRCEE for funding
- UK Environmental Research and Training Laboratory (ERTL) (John May & Tricia Coakley)
- UK Electron Microscopy Facility (Dr. Jia Ye)

Superfund Research Program

KRCEE Kentucky Research Consortium for Energy and the Environment

UK

Thank you!

Questions?