REDUCTIVE DECHLORINATION OF THE HERBICIDE ALACHLOR BY IRON NANOPARTICLES

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Civil Engineering Graduate Seminar

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Outline

- Background
- Objectives
- Experimental Methods
- Results
- Conclusions
- Remaining Work

Background: Iron Remediation

- Fe^0 is a potential reducing agent
- Many environmental contaminants are susceptible to reduction reactions
- Iron is non-toxic and inexpensive

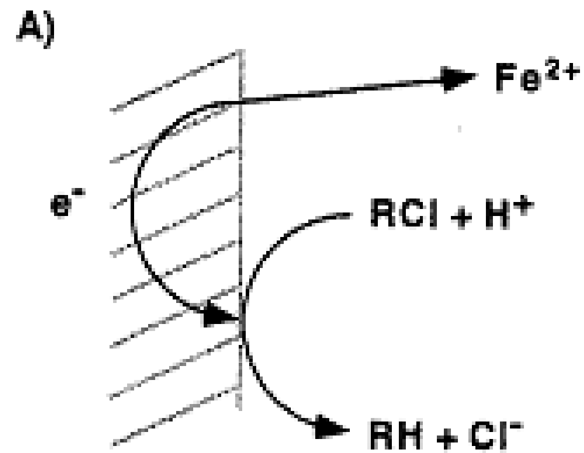


Image Credit: Matheson, L.J., Tratnyek, P.G., 1994. Environ. Sci. Technol. 28, 2045-2053.

Background: Iron Redox

- Redox Reactions:

  $Fe^{2+} + 2e^{-} \leftrightarrow Fe^{0}$ -0.440 V

  $Fe^{0} + RX + H^{+} \rightarrow Fe^{2+} + RH + X^{-}$

- Competing Reactions:

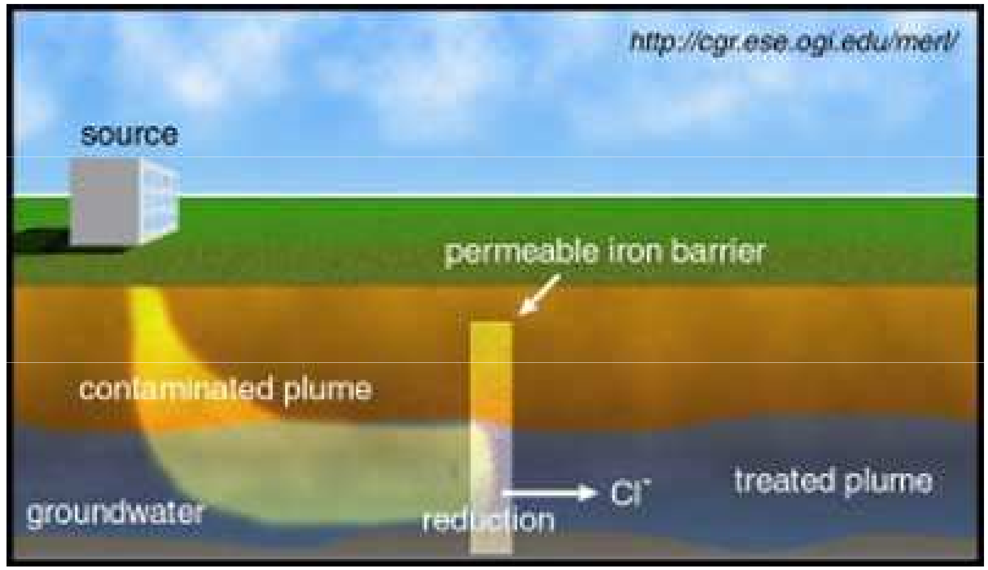
  $2Fe^{0} + O_2 + 2H_2O \leftrightarrow Fe^{2+} + 4OH^{-}$

  $Fe^{0} + 2H_2O \leftrightarrow Fe^{2+} + H_2 + 2OH^{-}$

Background: Iron Filings

- Research focused on chlorinated hydrocarbons (e.g., TCE)

- Successfully implemented in the field as permeable reactive barriers



Background: NanoZVI (nZVI)

- Late 1990s: rash of research in nZVI
- Laboratory results were outstanding
- Field studies have shown moderate success

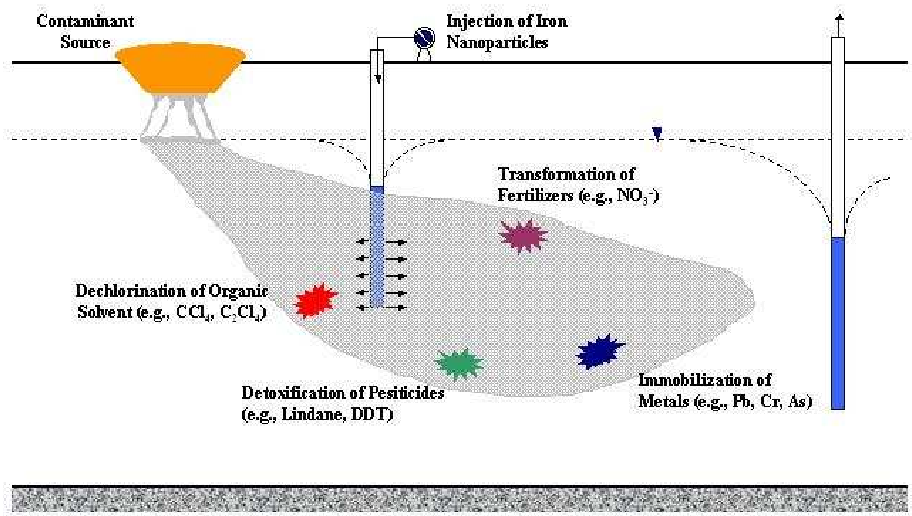


Image Credit: Zhang, W-X., 2003. J. Nanopart. Res. 5, 323-332.

nZVI: Reaction Speed

- Faster reactions with fewer potentially toxic byproducts
- Improvements in orders of magnitude are possible

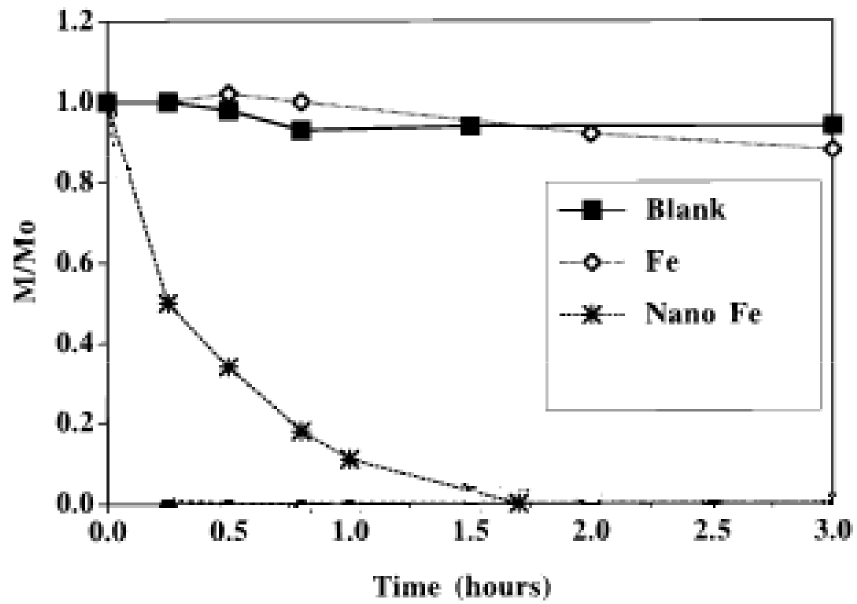


Image Credit: Wang, C.B., Zhang, W.X., 1997. Environ. Sci. Technol. 31, 2154-2156.

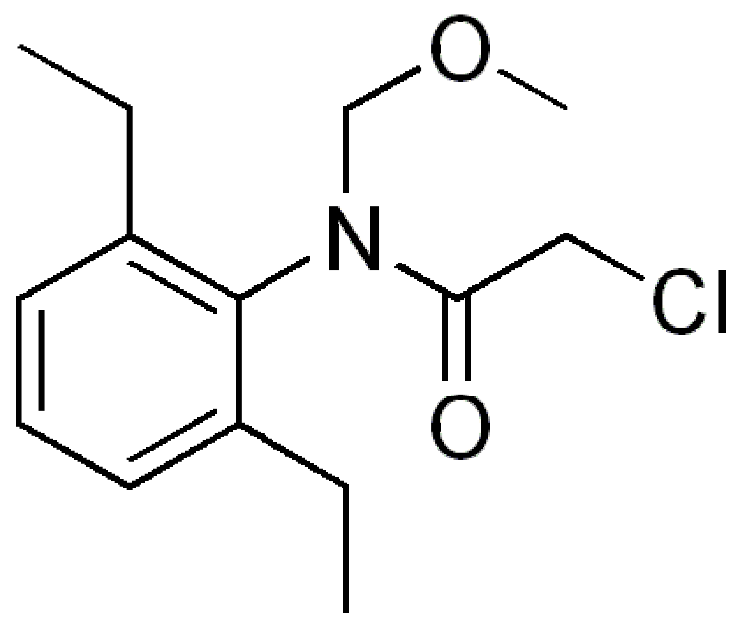
nZVI: Economics

Image Credit :http://www.vironex.com

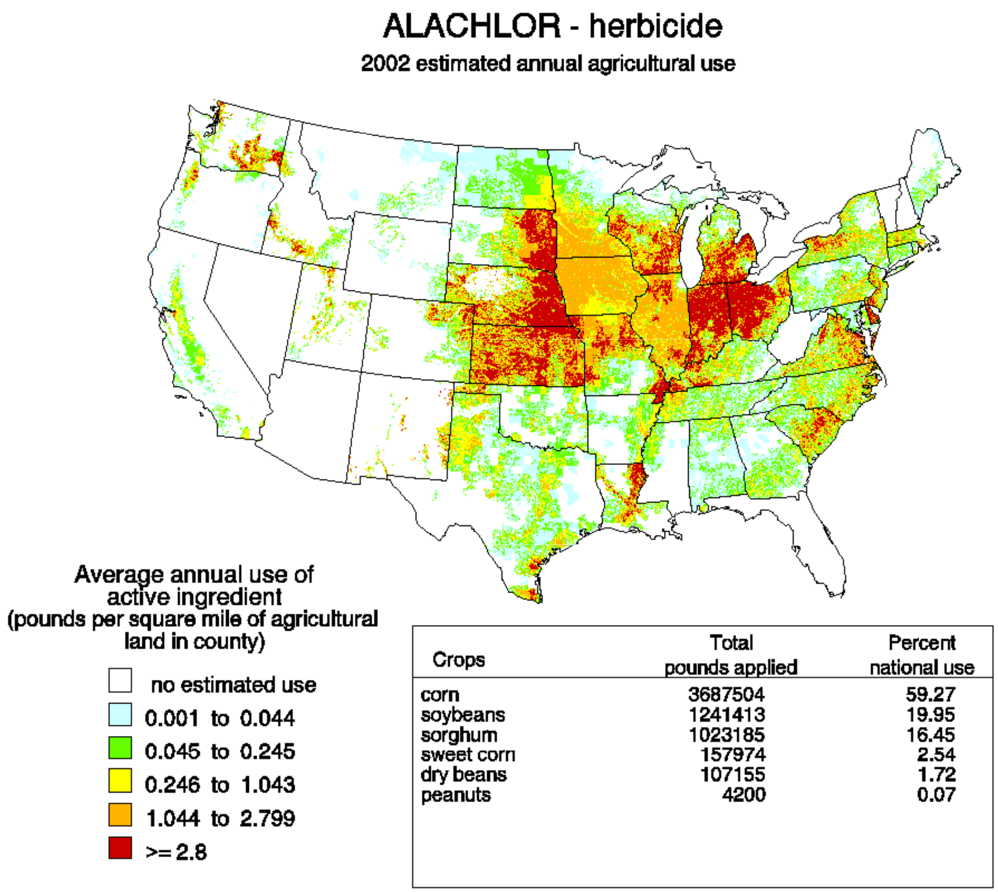
Image Credit :http://www.science.uwaterloo.ca

Background: Alachlor

- Herbicide for the control of grasses/weeds in corn and soybeans
- Maximum Contaminant Level (MCL) = 2 ppb
- Maximum Contaminant Level Goal (MCLG) = Zero
- Liver, kidney, spleen damage; cancer



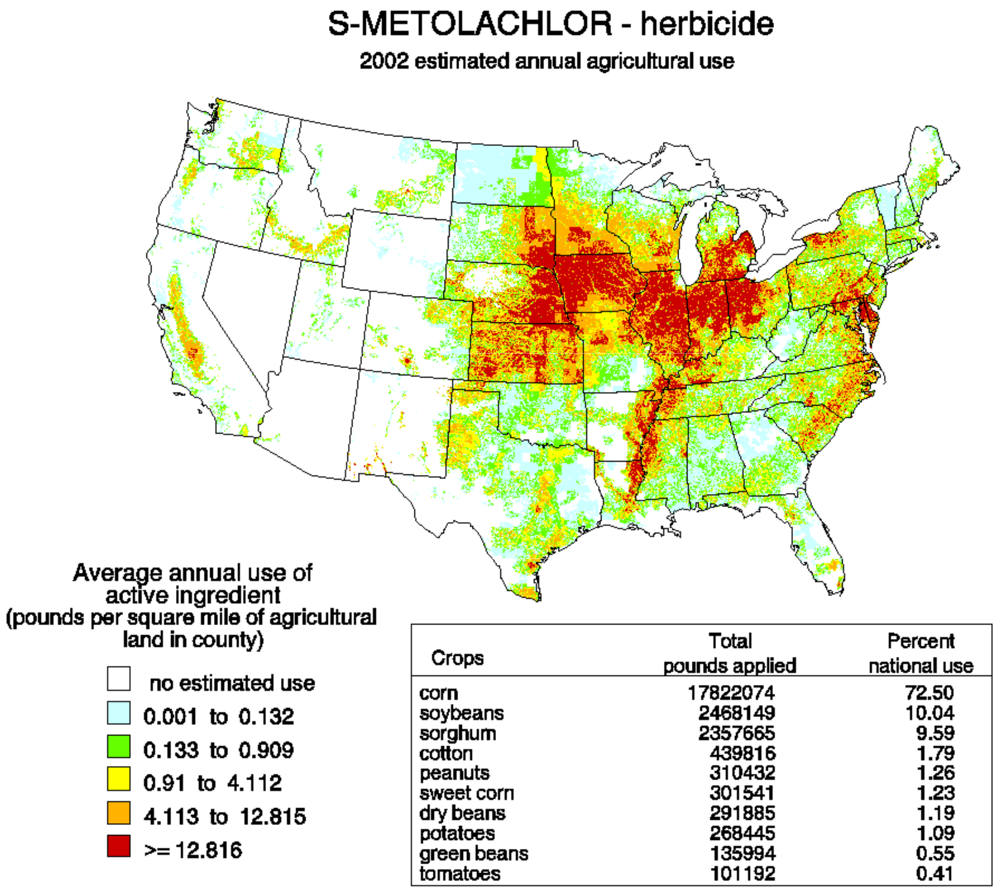
Background: Alachlor



Crops	Total pounds applied	Percent national use
corn	3687504	59.27
soybeans	1241413	19.95
sorghum	1023185	16.45
sweet corn	157974	2.54
dry beans	107155	1.72
peanuts	4200	0.07

Image Credit: United States Geological Survey (USGS)

Background: Alachlor



Crops	Total pounds applied	Percent national use
corn	17822074	72.50
soybeans	2468149	10.04
sorghum	2357665	9.59
cotton	439816	1.79
peanuts	310432	1.26
sweet corn	301541	1.23
dry beans	291885	1.19
potatoes	268445	1.09
green beans	135994	0.55
tomatoes	101192	0.41

Image Credit: United States Geological Survey (USGS)

Objectives

- To synthesize and characterize nanoscale iron
- To find kinetic parameters for alachlor degradation
- To identify reaction byproducts
- To compare nano iron with commercial iron

Experimental Methods

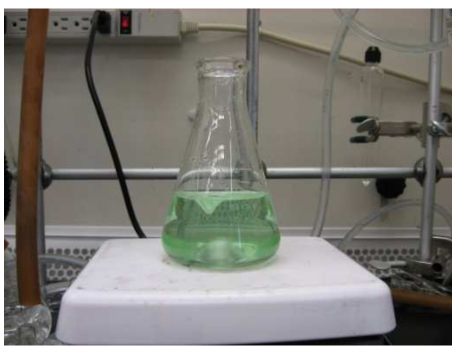
- Iron nanoparticle synthesis
  - Synthesis method
  - Particle characterization
- Kinetic trials
  - Experimental method
  - Results

nIron Synthesis

- Synthesis method: borohydride reduction

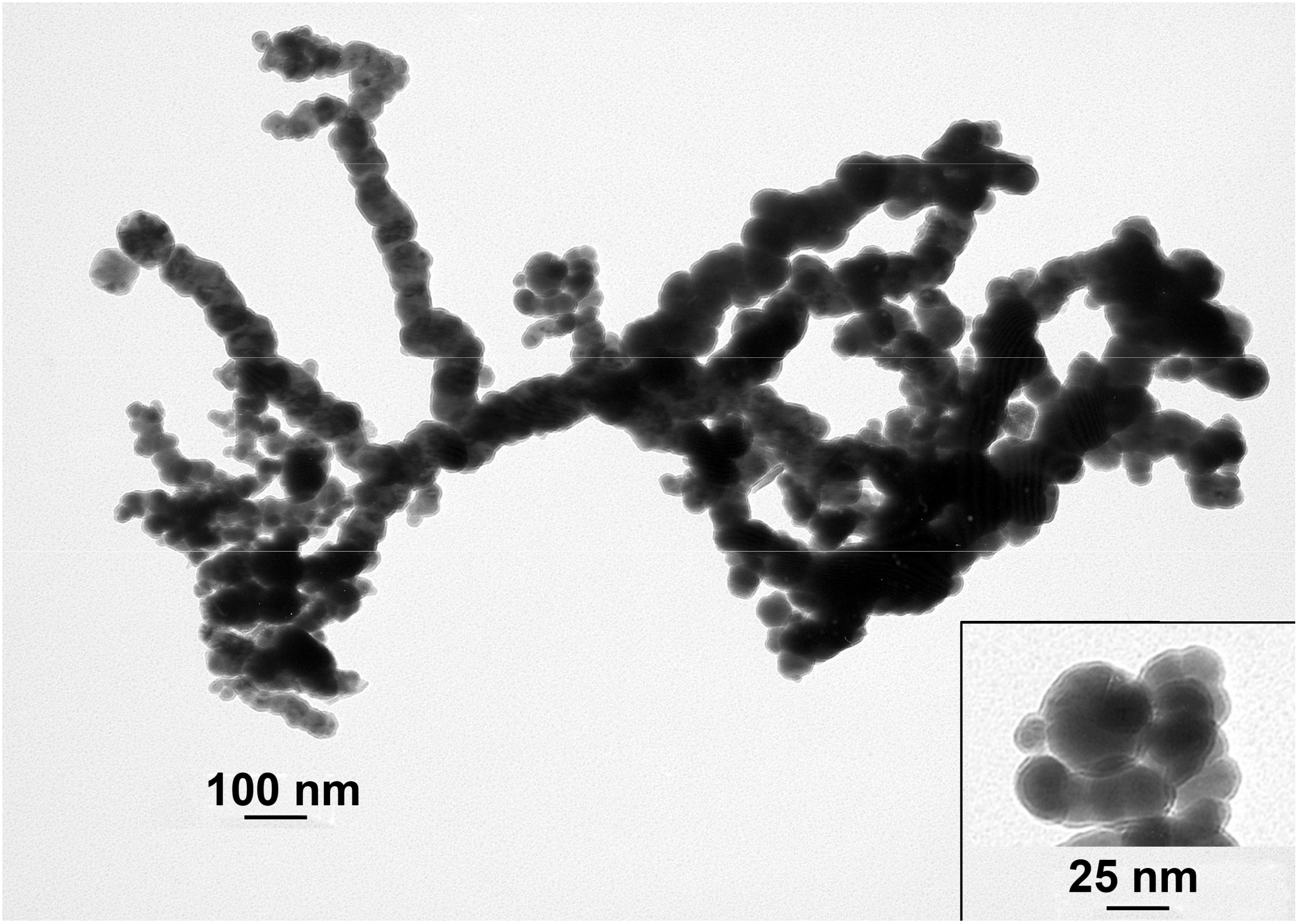
  $2Fe^{2+} + BH^{4-} + 3H_2O \rightarrow 2Fe^{0}\downarrow + H_2BO^{3-} + 4H^{+} + 2H_2$ [1]

- Method is safe, inexpensive and well-studied.

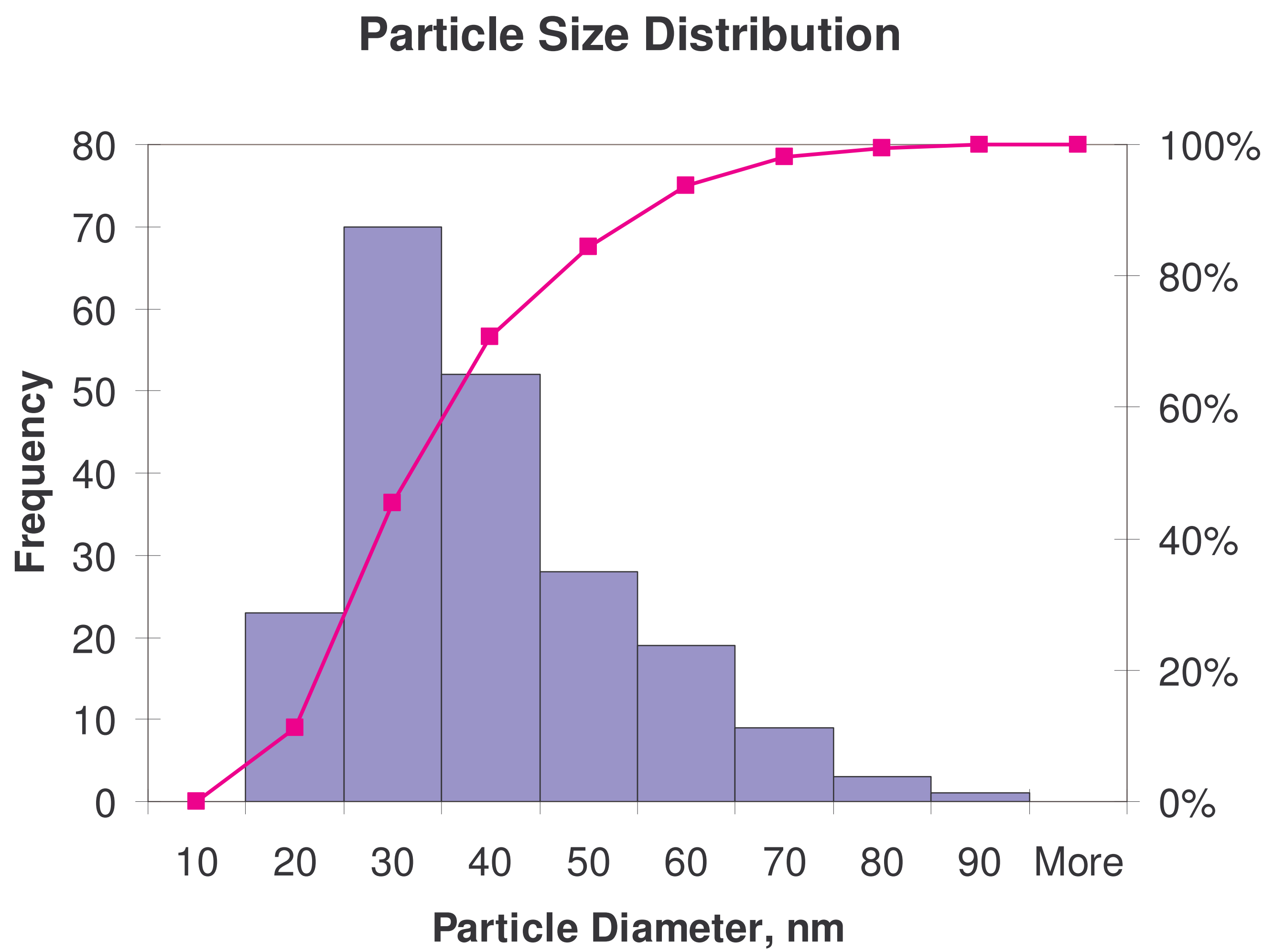


[1] Liu, Y., Majetich, S.A., Tilton, R.D., Sholl, D.S., Lowry, G.V., 2005. *Environ. Sci. Technol*. 39, 1338-1345.

nIron Characterization

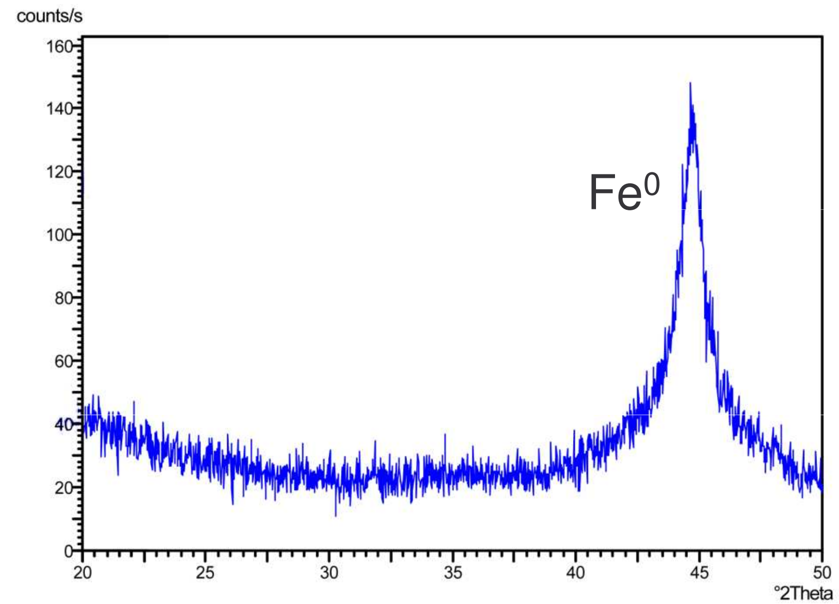


nIron Characterization



nIron Characterization

- XRD detects no iron oxides (typical corrosion products are hematite and magnetite)
- BET surface area analysis determined specific surface area to be 26 m^2/g



nIron Characterization: Summary

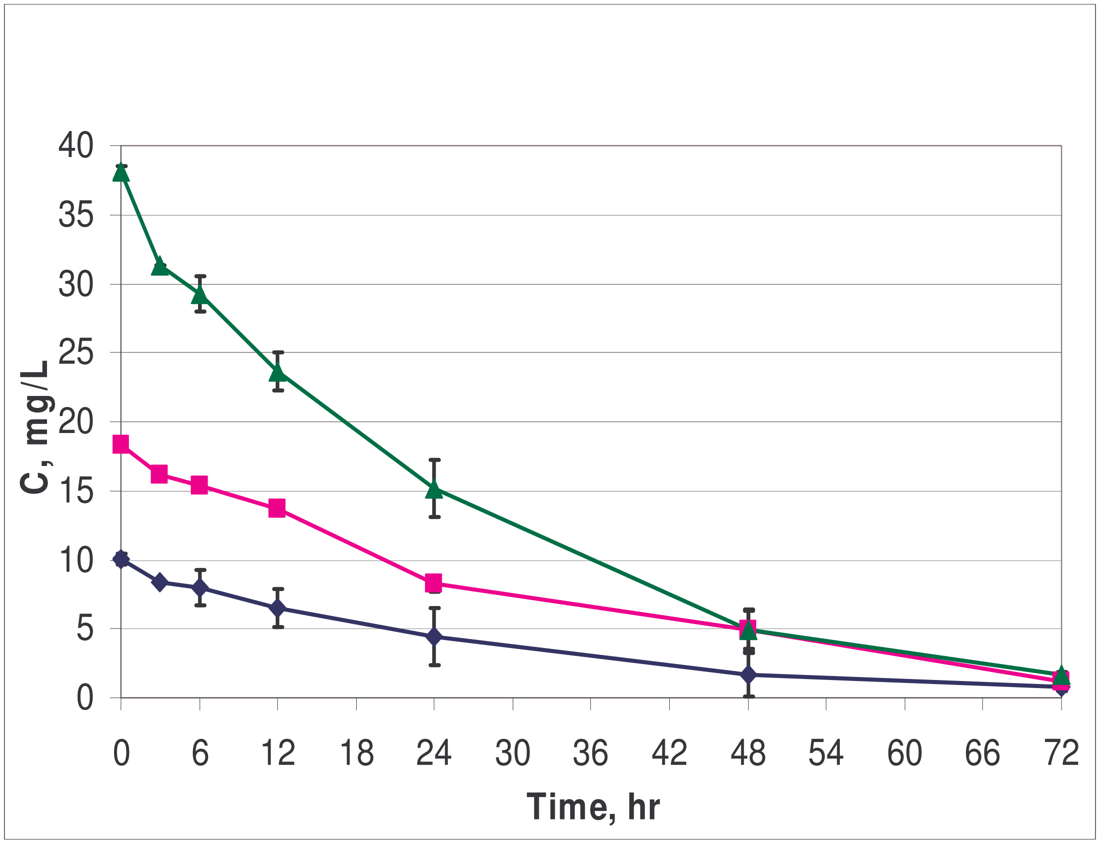
Physical Property	Reported Values (all NZVI)	Reported Values (NZVI, BH only)	Observed Values
Mean Particle Size (nm)	2-200	20-70	35
BET Surface Area (m^2/g)	15-60	20-55	26
Shell Thickness (nm)	1-20	2-3	~2.5

Kinetic Studies

- Varying iron loading and alachlor spike levels in deoxygenated/deionized water

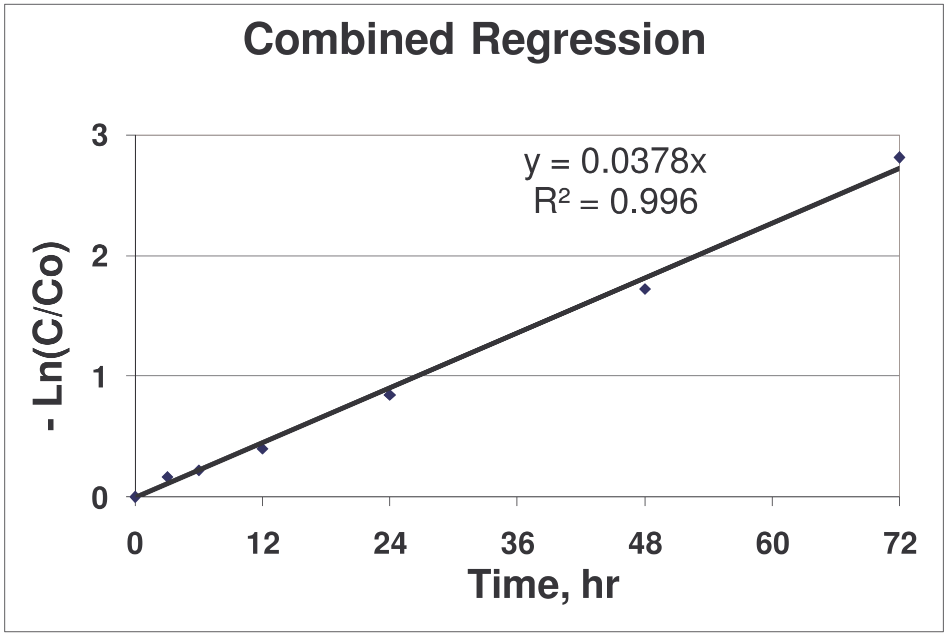
- Aliquots withdrawn at definite intervals and analyzed using HPCL, GC/MS or IC

Results: Kinetics



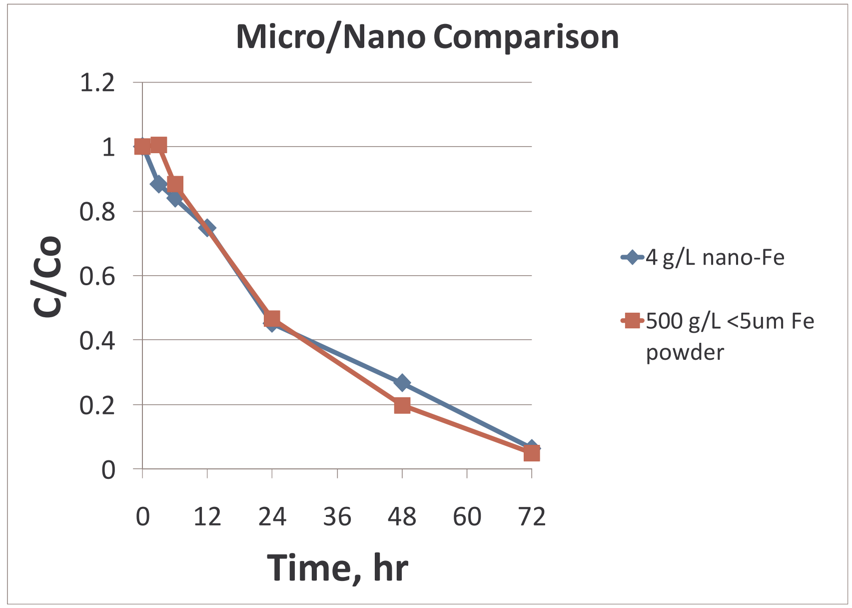
Results: Kinetics

- 1^{st} order reaction (pseudo 1^{st} order)
- $d[\mathbf{C}]/dt = \boldsymbol{k}_{\mathbf{obs}}[\mathbf{C}] = \boldsymbol{k}_{\mathbf{SA}}\ \rho_a\ [\mathbf{C}]$
- $\boldsymbol{k}_{\mathbf{SA}} = 3.63 \times 10^{-4}$ L m^{-2} h^{-1}

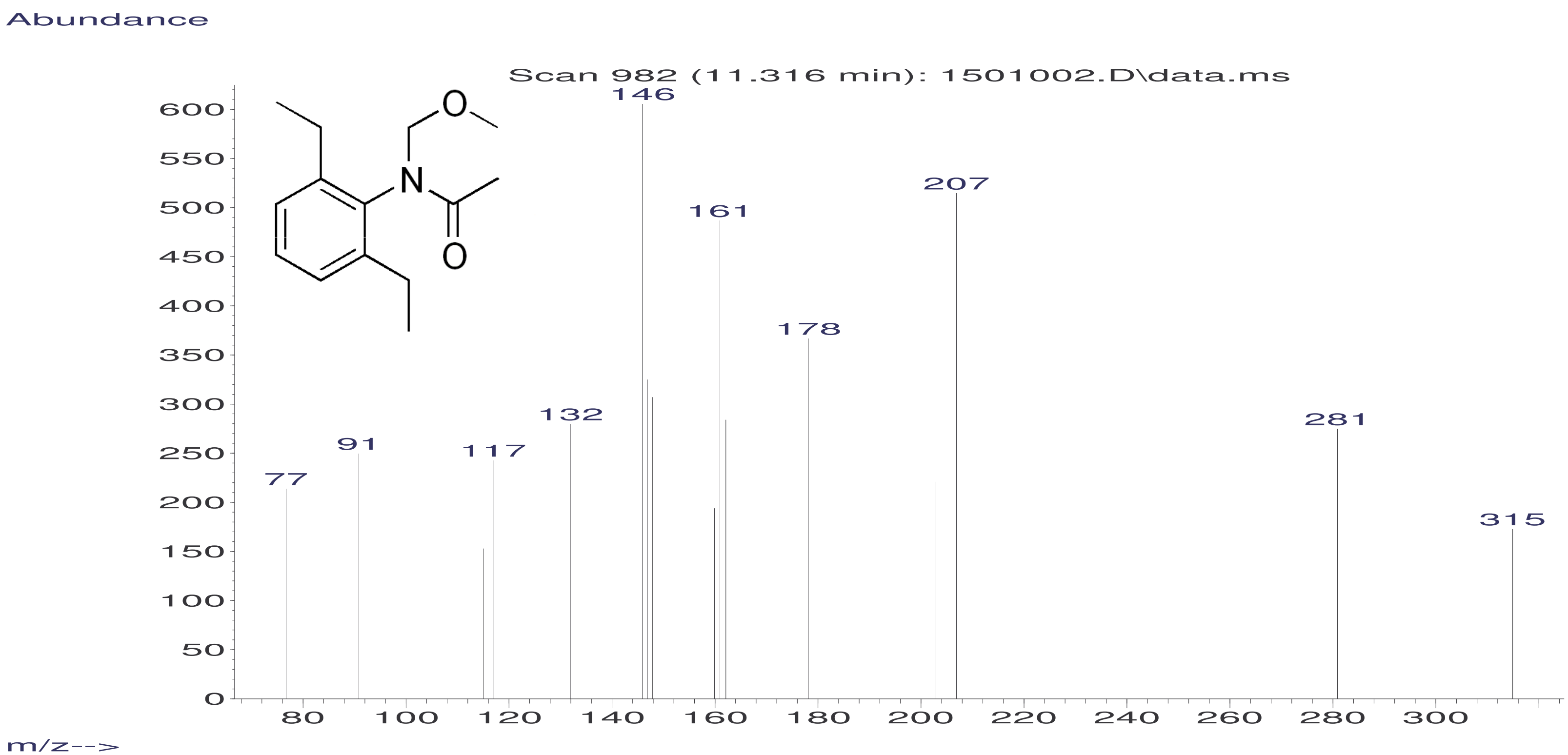


Results: Kinetics

- 500g/L micro iron vs 4g/L nano iron
- $k_{SA,\ micro} = 0.77 \times 10^{-4}\ \mathrm{L\ m^{-2}\ h^{-1}}$
- $k_{SA\ nano} = 3.63 \times 10^{-4}\ \mathrm{L\ m^{-2}\ h^{-1}}$
- Thus, nano Fe reacts roughly 5 times faster, even when normalized for surface area



Results: Byproduct



Conclusions

- Iron nanoparticles represent a marked improvement over iron powder and filings
- Potential applications
  - Spill remediation
  - On-site treatment
  - <u>Caveat</u>: Byproduct's toxicology and biodegradability are unknown

Remaining Work

- Iron loading trial: further runs and data analysis
- Ion chromatography: Cl^- mass balance
- More pesticides
- Further applications

Previous Presentations

Thompson, J., Bezbaruah, A., Chisholm, B., June 25 2007. Laboratory Scale Study to Determine the Effectiveness of Iron Nanoparticles for Selected Pesticide Remediation. AWRA Summer Specialty Conference. Vail, CO. [Poster]

Thompson, J., Elorza, J., Bezbaruah, A., Chisholm, B., August 3 2007. Iron Nanoparticles for the Treatment of the Herbicides Atrazine, Alachlor and Dicamba in Groundwater. ATINER 2nd International Symposium on Environment. Athens, Greece. [Presentation]

Thompson, J., Bezbaruah, A., Chisholm, B., December 11 2007. Rapid Dechlorination of the Herbicide Alachlor by Zero Valent Iron Nanoparticles. ISNEPP 2007 Nanotechnology in Environmental Protection and Pollution. Ft. Lauderdale, FL. [Presentation, Accepted]

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