EFFECTIVE DELIVERY OF IRON NANOPARTICLES USING AMPHIPHILIC POLYSILOXANE GRAFT COPOLYMERIC VEHICLES

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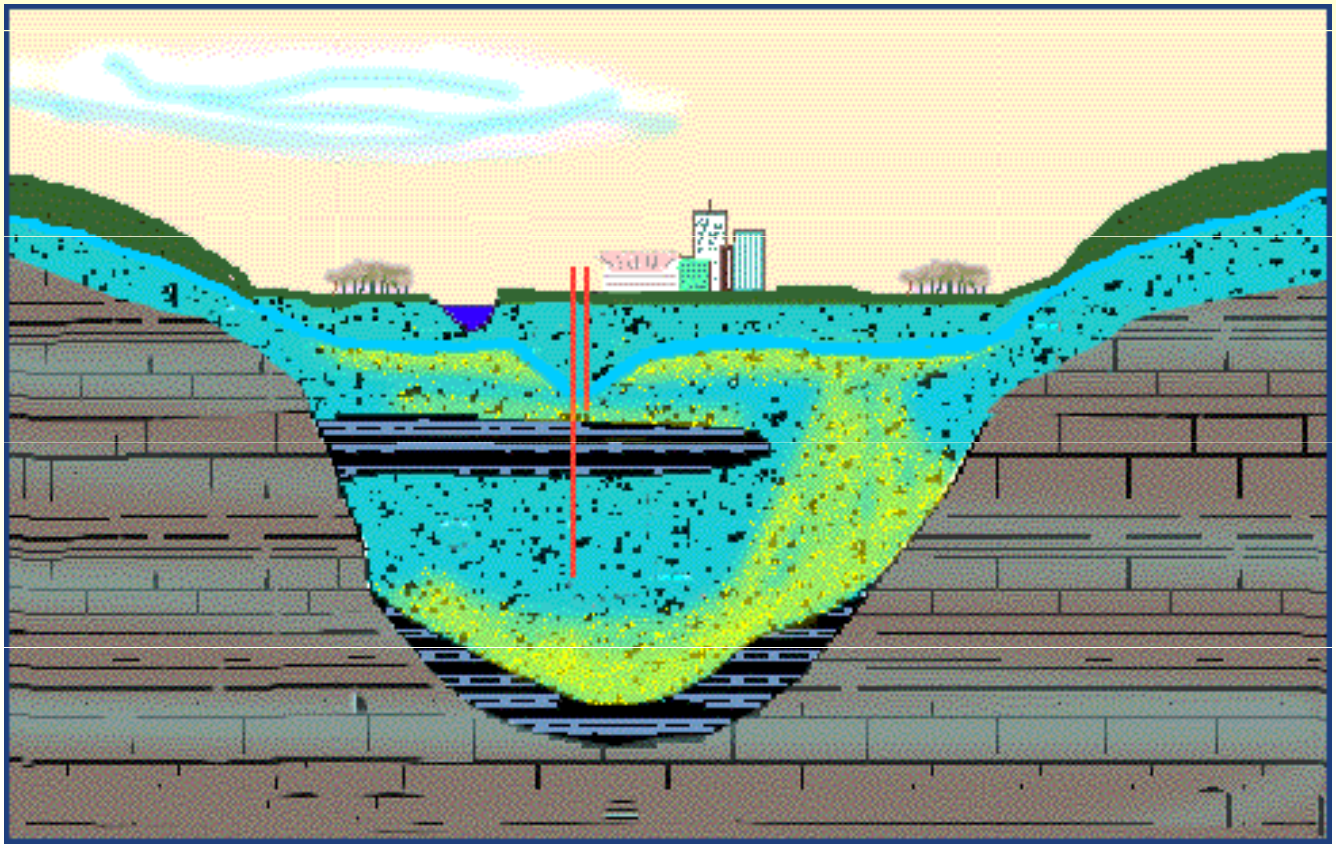
OUTLINE

- Background
- Objectives
- Hypothesis
- Research Approach
- Results
- Summary

BACKGROUND

Groundwater Contamination



http://www.gwconsortium.org/

BACKGROUND

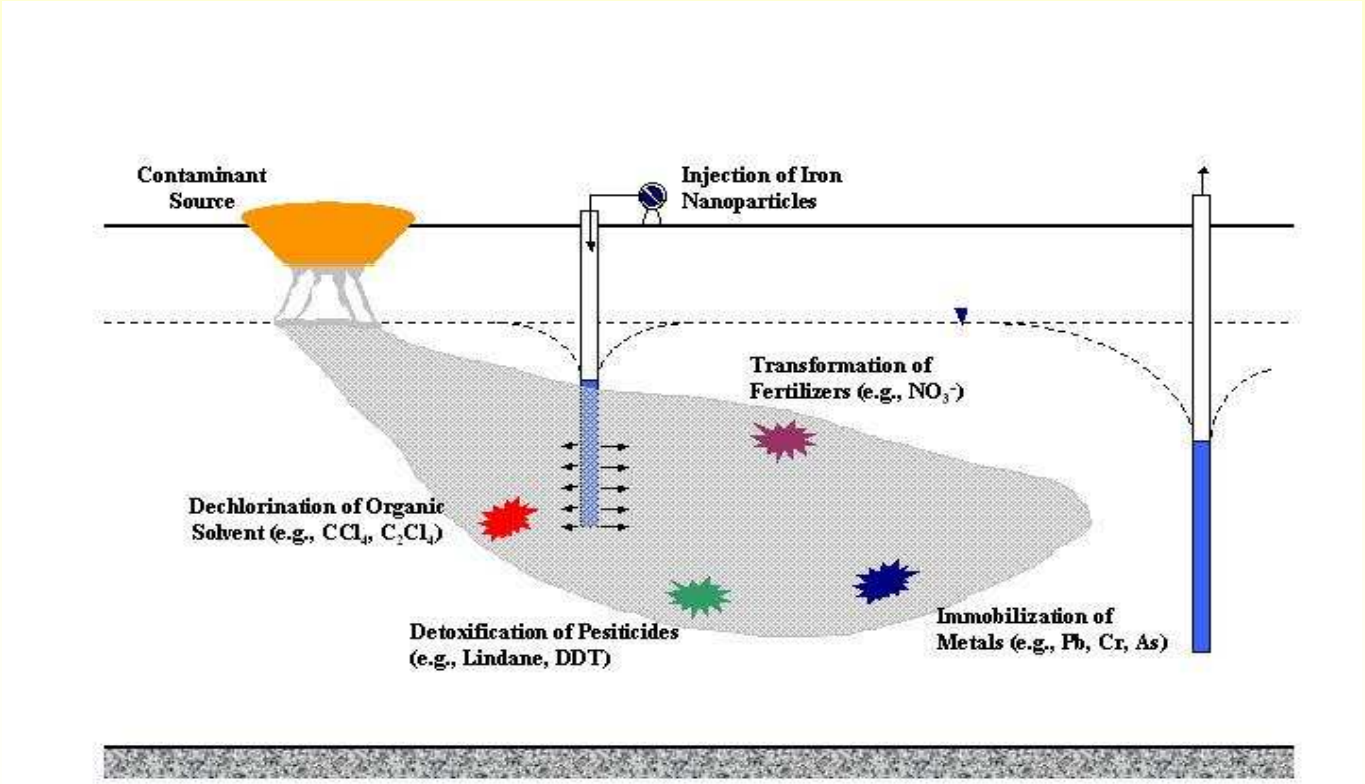
Groundwater Remediation

- Biological treatment
  - Inexpensive
  - Takes long time
- Physical/Chemical treatment
  - Very fast technique
  - Slightly expensive

http://www.gwconsortium.org/

BACKGROUND

Injection of Zero-valent Iron Nanoparticles (nZVI)

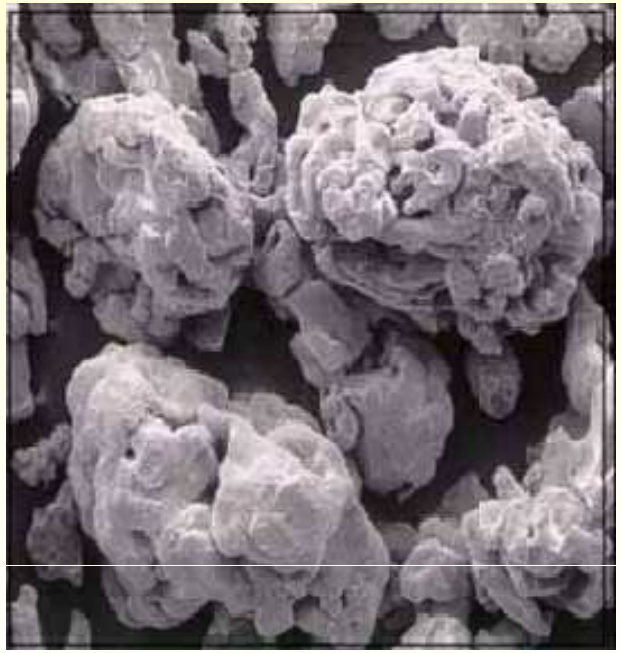


http://www.nsf.gov/

BACKGROUND

Why Iron Nanoparticles?

- Highly effective on several kinds of reducible contaminants
- Easy in dispersion to all spaces available (subsurface injection)
- High reactive surface area (~35 m^2/g)
- Extremely high reaction rate
- Low temperature reaction
- Economics (relatively inexpensive)



http://enviro.nfesc.navy.mil/

BACKGROUND

Treatable with Iron Nonoparticles

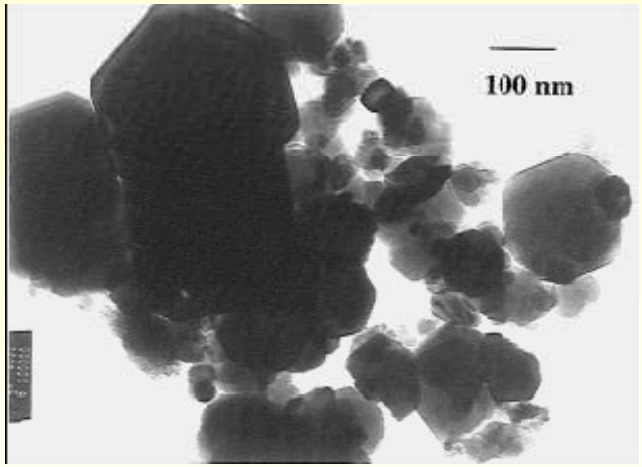
- **Methanes:**
  Carbon tetrachloride (CT)
  Chloroform
  Bromoform
- **Ethanes:**
  Hexachloroethane
  1,1,1-Trichloroethane (TCA)
  1,1,2,2-Trichloroethane
  1,1,2,2-Tetrachloroethane
  1,1,1,2-Tetrachloroethane
  1,1-Dichloroethane (DCA)
- **Ethenes:**
  Tetrachloroethene (PCE)
  Trichloroethene (TCE)
  1,1-Dichloroethene
  trans-1,2-Dichloroethene
  cis-1,2-Dichloroethene

  Vinyl chloride
- **Other Organics:**
  1,1,2-Trichlorotrifluoroethane (Freon 113)
  Trichloroflouromethane (Freon 11)
  1,2,3-Trichloropropane
  1,2-Dichloropropane
  1,2-Dibromo-3-chloropropane
  1,2-Dibromoethane
  n-Nitrosodimethylamine (NDMA)
  Nitrobenzene
- **Inorganics:**
  Chromium, nickel
  Lead, Copper, Zinc
  Nitrate , Arsenic

BACKGROUND

- **Zhang, *et al.* (1997)**

  Nanoscale particles can quickly and completely dechlorinate several chlorinated aliphatic compounds and mixture of polychlorinated biphenyls (PCB) at relatively low metal to solution ratio

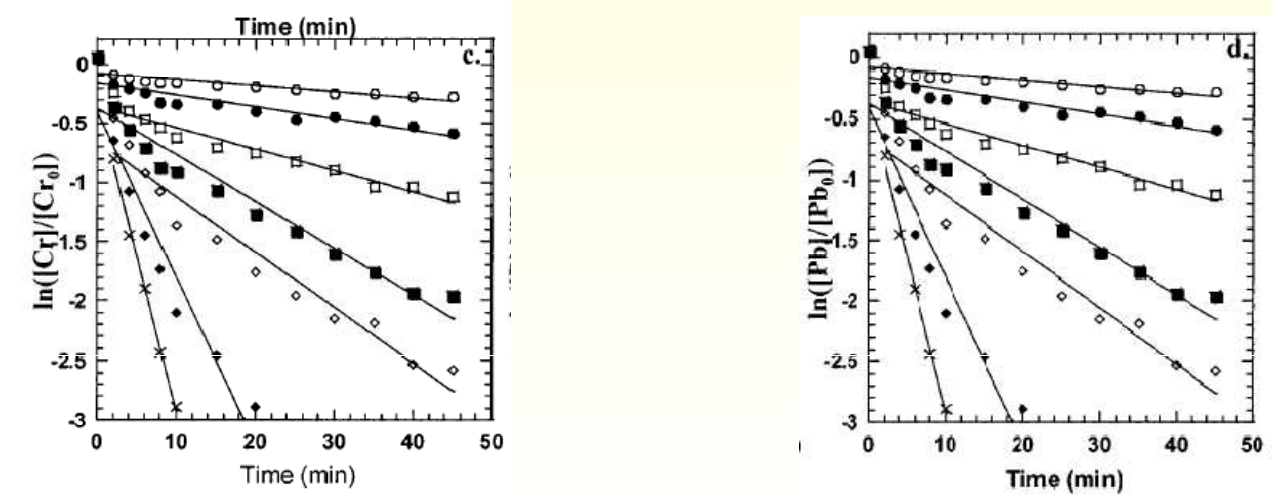


Transmission electron microscopy image of nanoscale Fe particles.

BACKGROUND

- **Ponder, *et al.*(2000)**

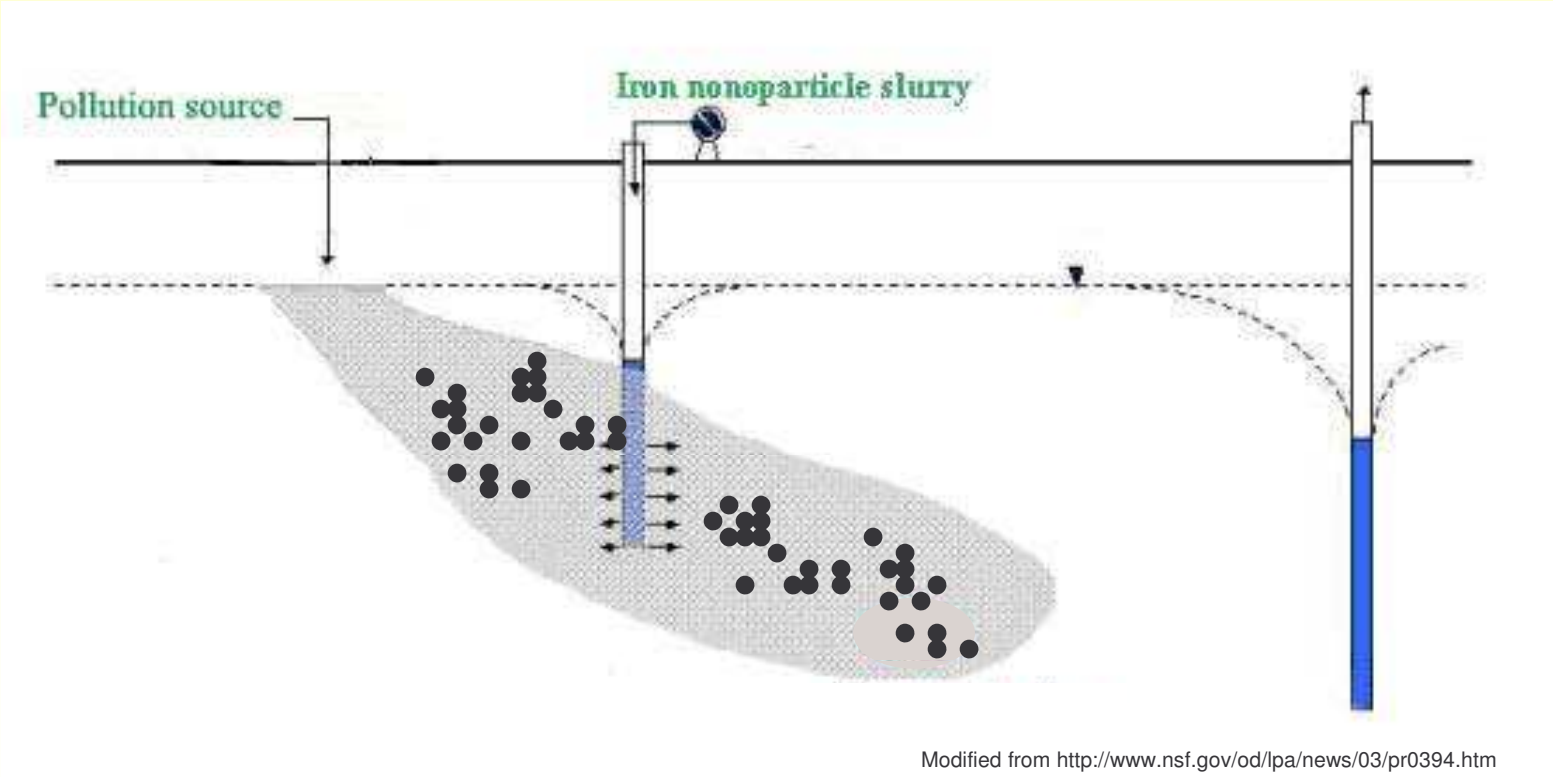
  nZVI rapidly immobilize Cr(VI) and Pb(II) in aqueous solution



Comparison of first-order kinetics for reduction of Cr(VI) and Pb(II)

BACKGROUND

In-Situ Remediation using nZVI



Modified from http://www.nsf.gov/od/lpa/news/03/pr0394.htm

Problems: Oxidation Rate ↑ and Dispersibility ↓

BACKGROUND

In-situ application for nZVI (state-of-the-art)

- Injection of a carbon source needed to

  - render the site anoxic

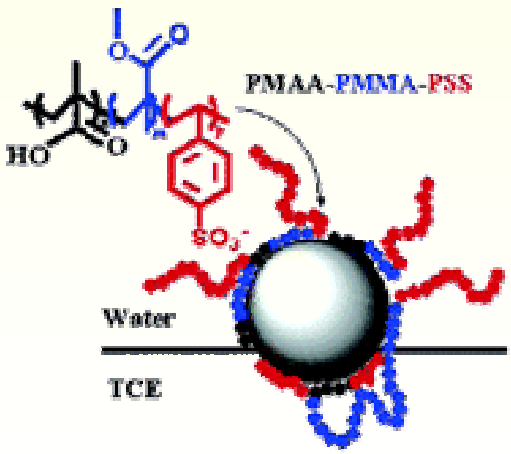
  - prevent oxidation of Fe° particles by non-targets

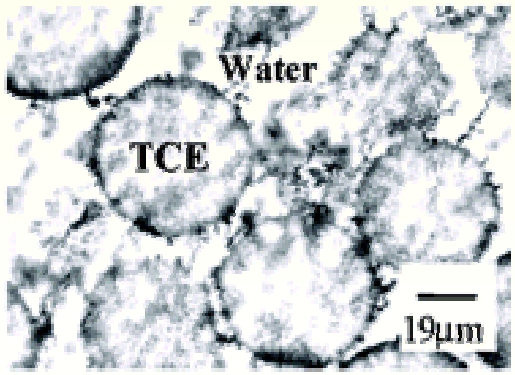
- High financial investment
- Time consuming

BACKGROUND

- **Saleh, *et al.* (2005)**

  Used novel triblock copolymers to modify iron nanoparticle surfaces for promoting colloidal stability in aqueous suspension and drive intothe oil/water interface

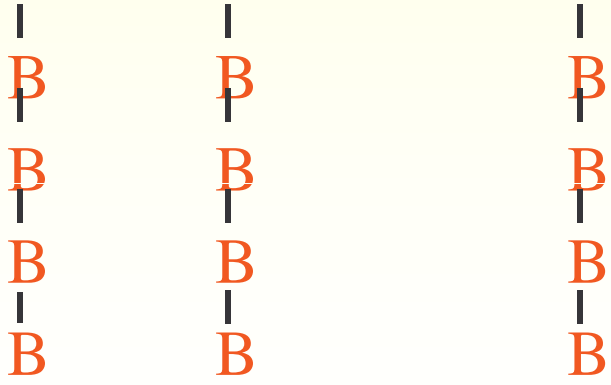




BACKGROUND

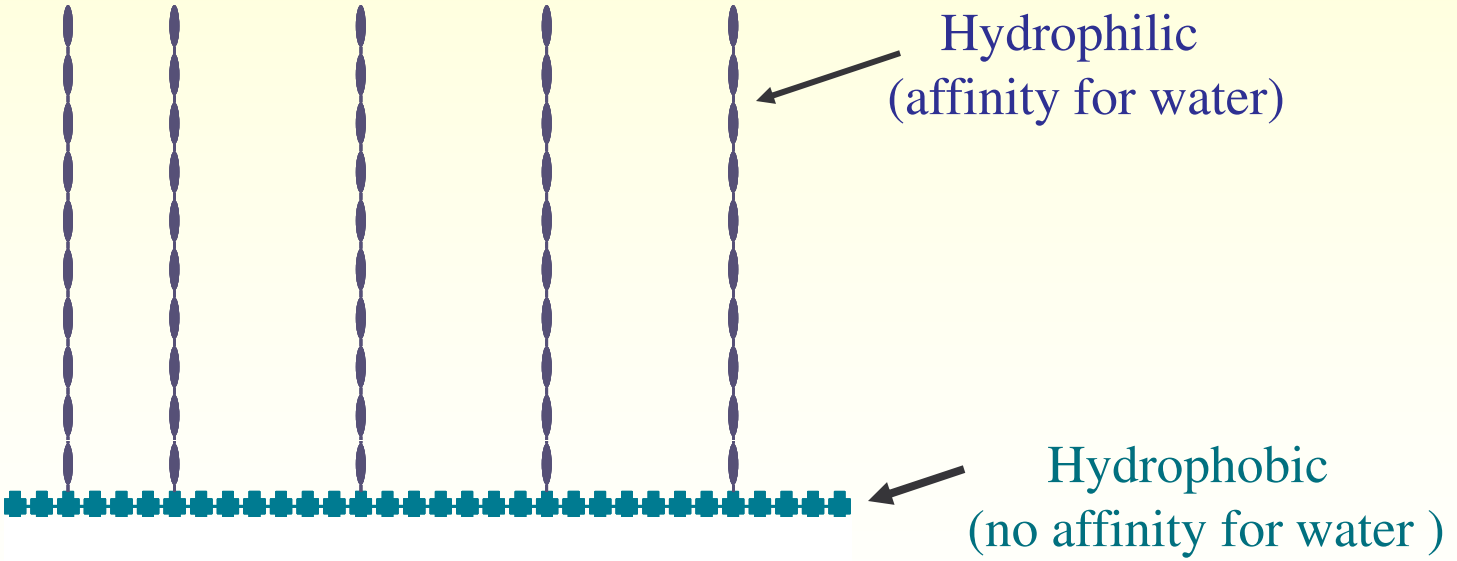
Type of Copolymers

- Random Copolymers : A-A-B-B-A-A-A-B-A-B-A-A-B-B-B
- Alternating Copolymers: A-B-A-B-A-B-A-B-A-B-A-B-A-B
- Block Copolymers: A-A-A-A-B-B-B-B-A-A-A-A-B-B-B…
- Graft Copolymers: A-A-A-A-A-A-A-A-A-A-A-A-A-A-A

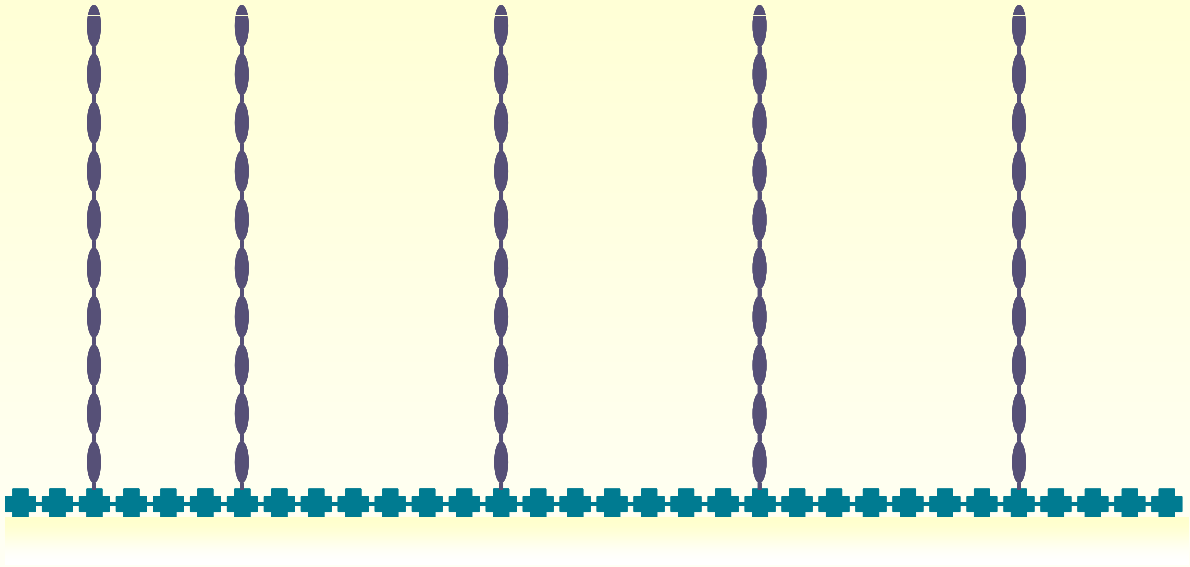


BACKGROUND

- Amphiphilic Graft Copolymer

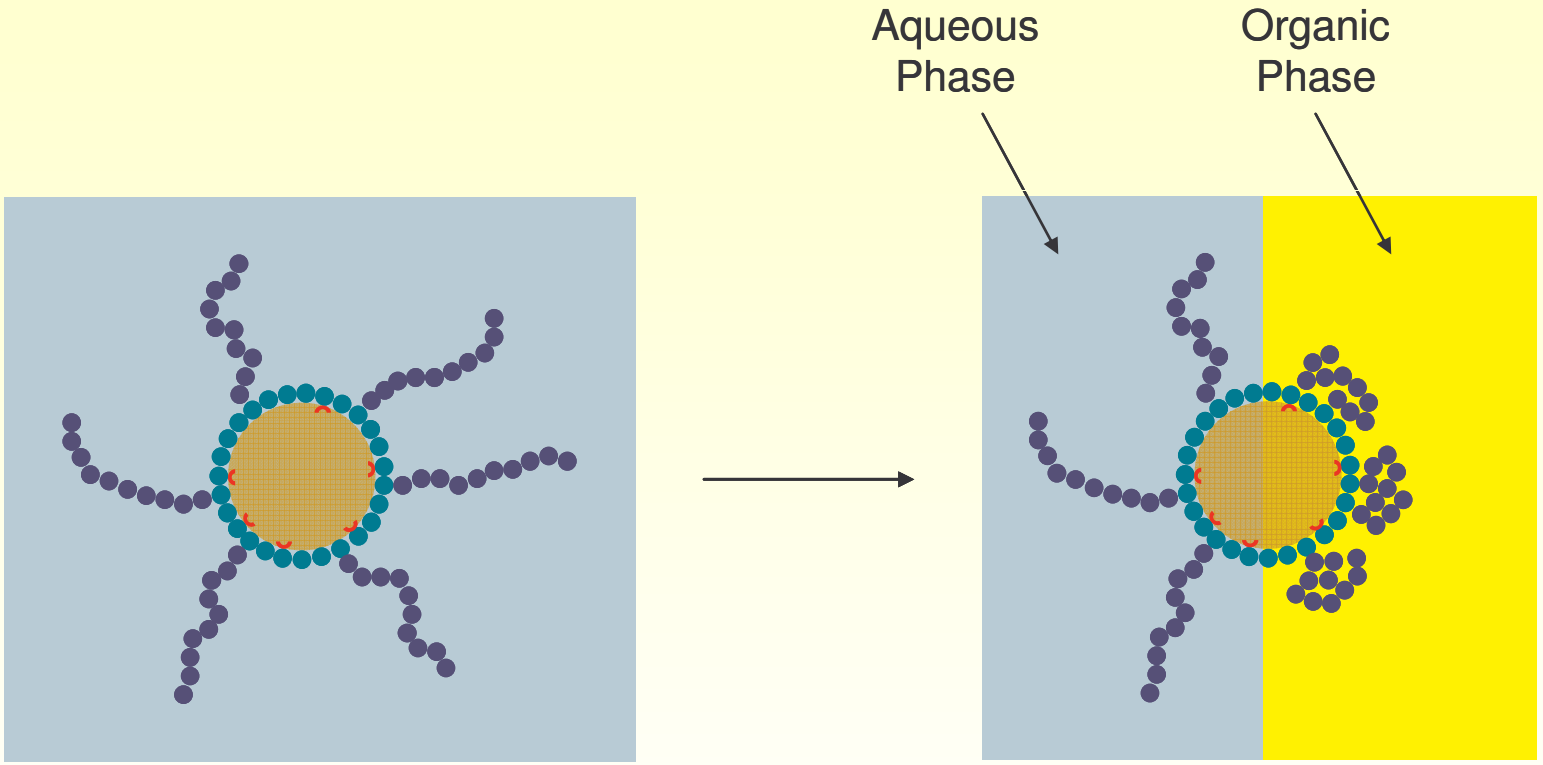


BACKGROUND



A schematic representation of amphiphilic polysiloxane graft copolymer (APGC)

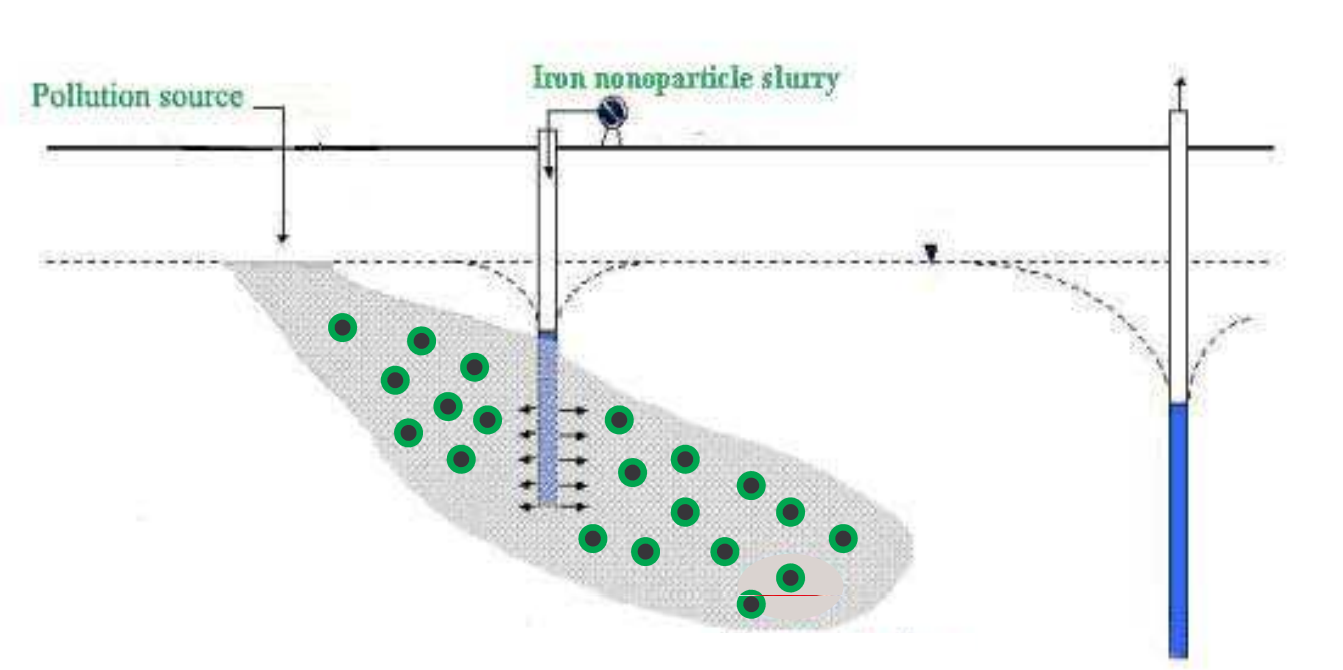
BACKGROUND



A schematic representation of the polymer coated nanoparticles both in water and at the water/contaminant interface.

BACKGROUND

In-Situ Remediation using polymer coated iron nanoparticles slurry



Modified from http://www.nsf.gov/od/lpa/news/03/pr0394.htm

Oxidation Rate ↓ and Dispersibility ↑

MAIN OBJECTIVE

Modify the Iron Nanoparticle surface using amphiphilic polysiloxane graft copolymer (APGC) to be effective for groundwater remediation

SPECIFIC OBJECTIVES

- Synthesis and characterization of APGCs
- Synthesis and characteristic of the iron nanoparticles
- Measurement of sedimentation rate and interface affinity of polymer coated iron nanoparticles
- Comparison of reaction kinetics during polymer coated and uncoated of iron nanoparticles mediated degradation of TCE (Trichloroethylene)
- Degradation of TCE by-products and corrosion of iron nanoparticles

HYPOTHESIS

Amphiphilic polysiloxane graft copolymers will provide the colloidal stability, protection against hydrolytic oxidation, and affinity for the water/ contaminant interface needed to improve capabilities of nZVI for groundwater remediation

RESEARCH APPROACH

- Task I : Synthesis and characterization of amphiphilic polysiloxane graft copolymers (APGC)
- Task II: Synthesis and characterization of nZVI
- Task III : High throughput measurement of sedimentation rate and interface affinity
- Task IV: Batch studies to compare the effectiveness of the polymer coated and bare nZVI for TCE degradation
- Task V: By-products of TCE and characterization of nZVI

TASK I : Synthesis/Analysis of APGC

Nuclear Magnetic Resonance Spectroscopy (NMR)

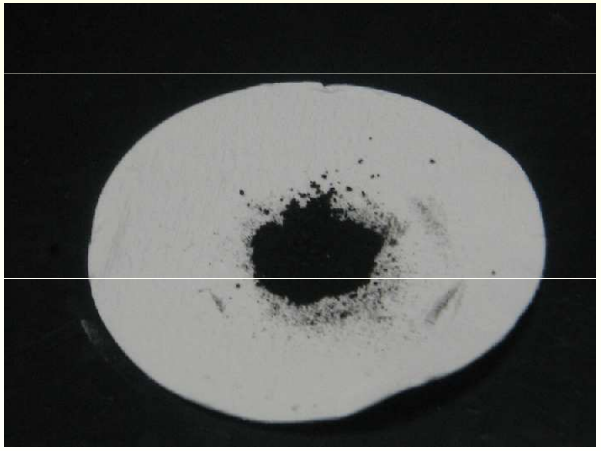
Fourier Transform Infra Red spectroscopy (FTIR)

(chemical structure of polymers)

TASK II : Synthesis of nZVI

Using method by Liu, *et al.* (2005)

- Sodium borohydride is the key reductant
- $NaBH_4$ is added to $FeSO_4.7H_2O$
- N_2 environment

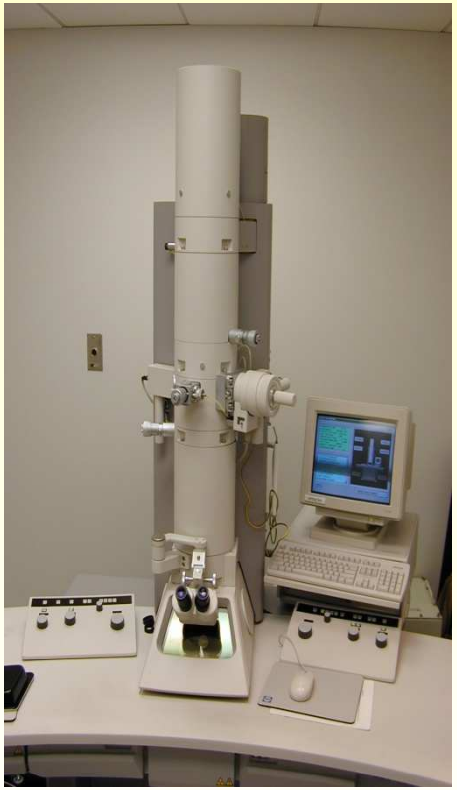


Iron nanoparticles

Glove Box

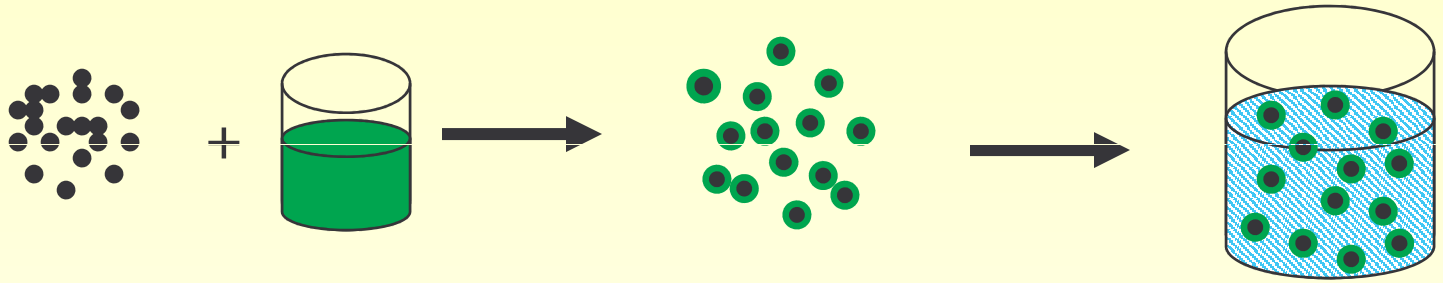
TASK II : Analysis of nZVI

X-ray diffraction (XRD)
(composition of the nanoparticles)



Transmission electron microscope (TEM)
(size distribution of the nanoparticles)

TASK III: Colloidal Study



UV Spectrophotometer

TASK IV : Kinetic Studies

- Contaminant: TCE
- Batch test using polymer coated and bare nZVI

  - 20 mL vials used as a batch reactor

  - Control studies done

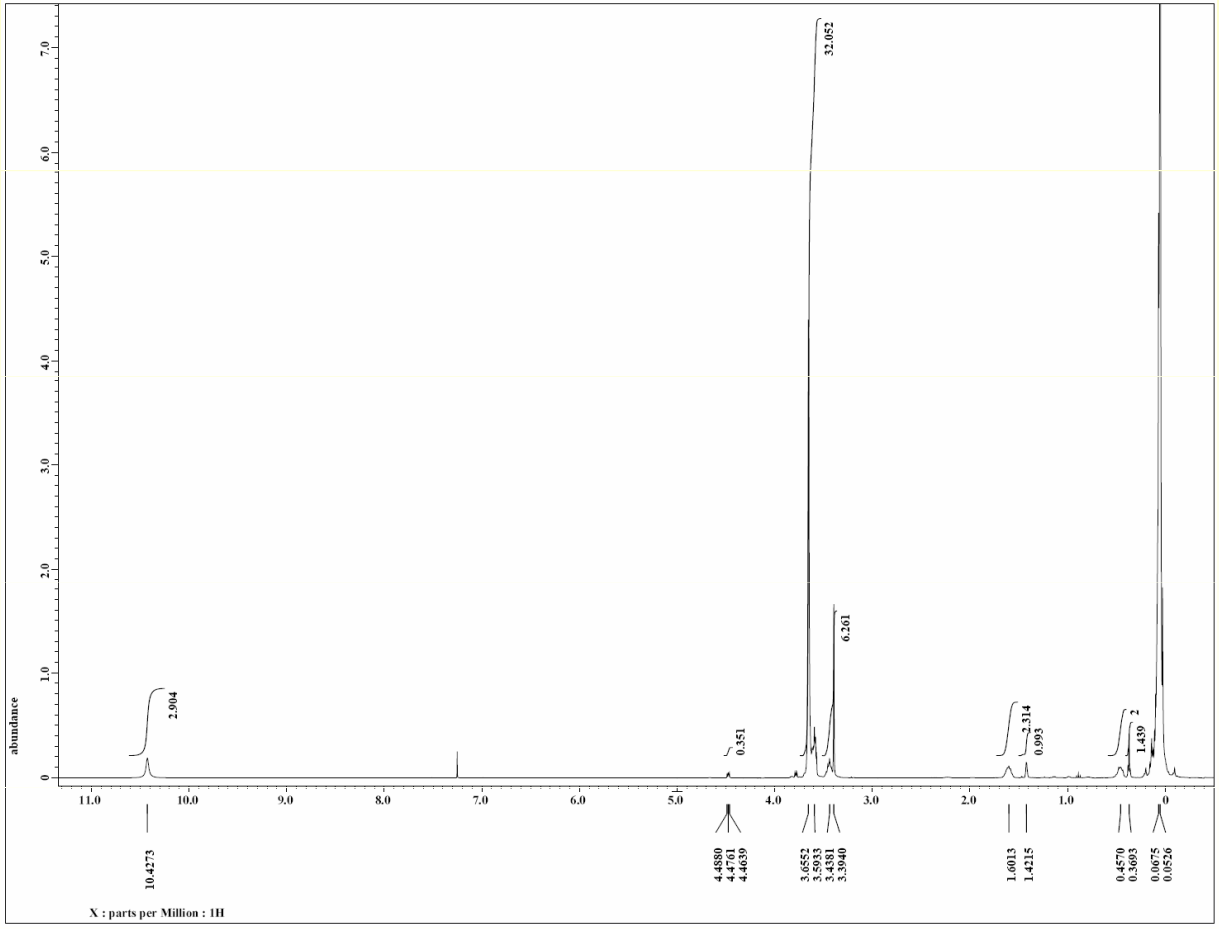
Gas Chromatography-Mass Spectrometry (GC-MS)

TASK V : TCE by-products and characterization of Fe°

Gas Chromatography-Mass Spectrometer (GC-MS)

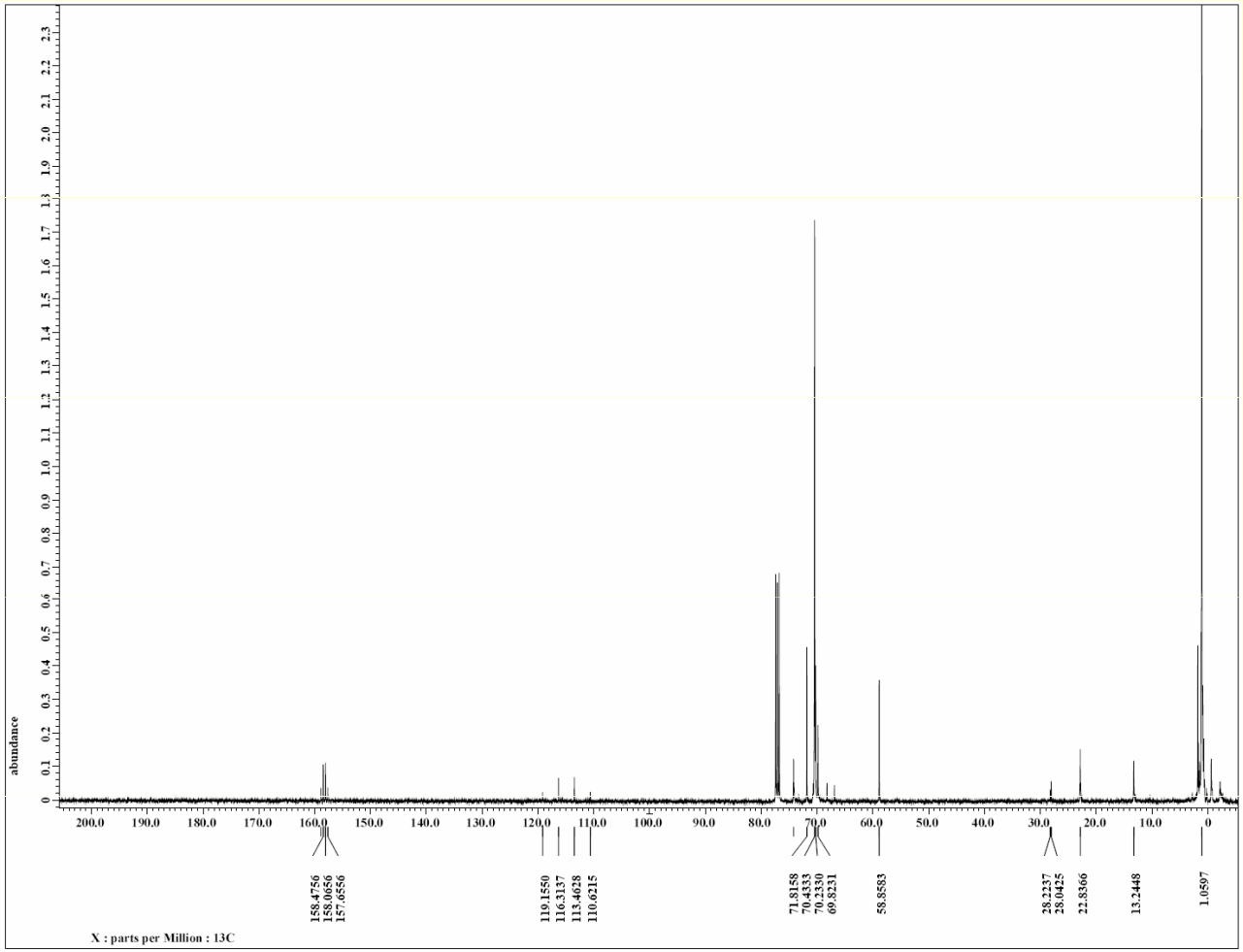
Scanning Electron Microscopy (SEM) / EDX

RESULTS …Task I : Synthesis of APGC



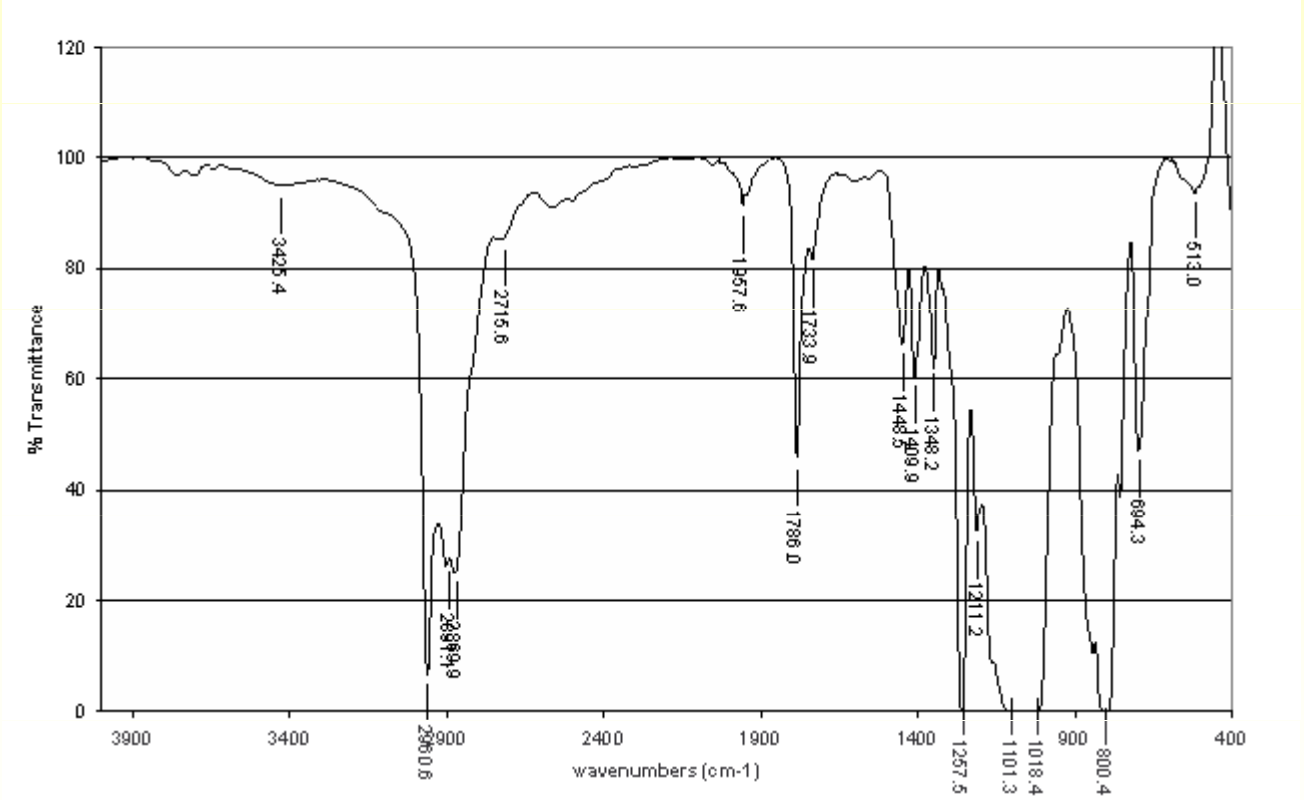
^{1}H NMR of PEG-AA-PDMS

RESULTS …Task I : Synthesis of APGC



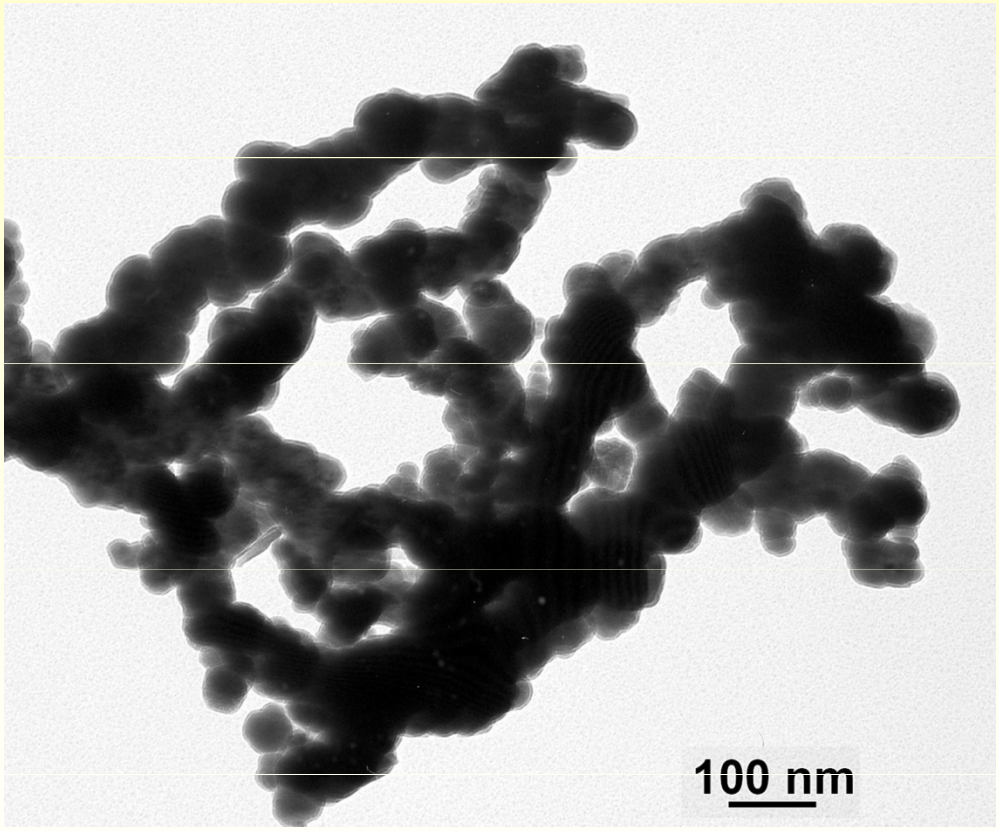
^{13}C NMR of PEG-AA-PDMS

RESULTS …Task I : Synthesis of APGC



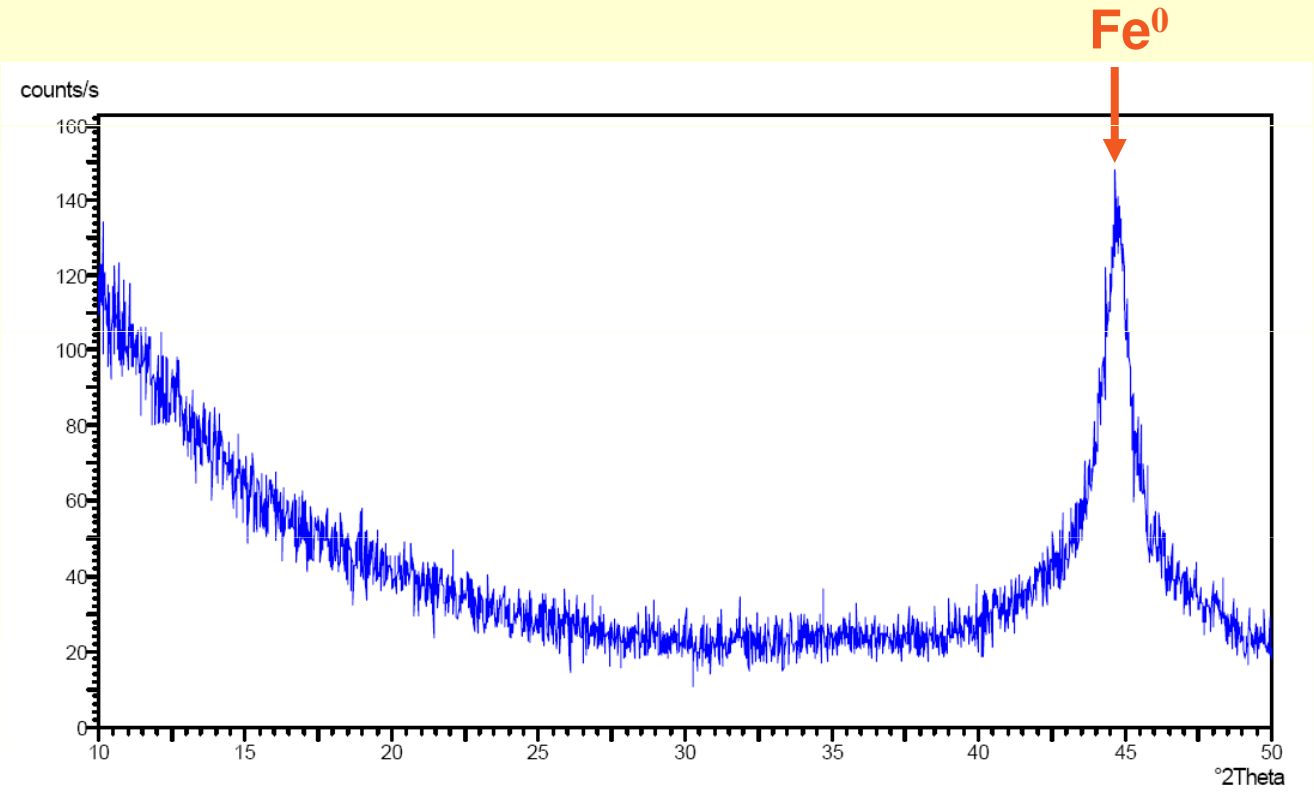
FTIR spectra of PEG-AA-PDMS

RESULT…TASK II : Synthesis of nZVI



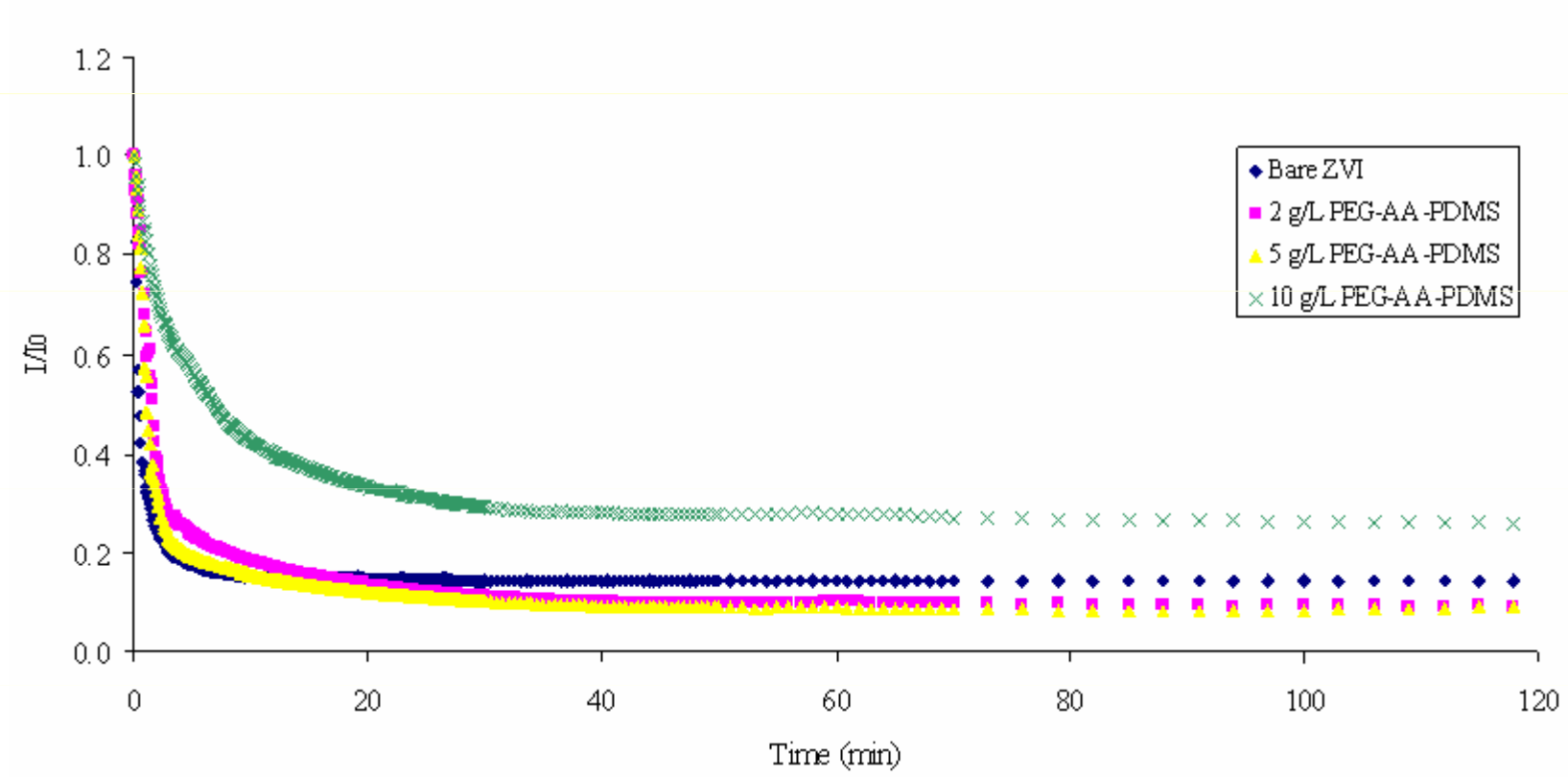
TEM image of Fe^0 nanoparticles

RESULT…TASK II : Synthesis of nZVI



XRD spectra of Fe^0 nanoparticles

TASK III: Colloidal Stability Study



Use of 10g/L of APGC gives the best colloidal stability to nZVI

SUMMARY

- Task I : Synthesis of APGC
  - This task is already completed
- Task II: Synthesis of Fe° Nanoparticles
  - This task is already completed
- Task III: Colloidal Study
  - Working on various APGCs and modified nZVIs
- Task IV: Kinetic Studies
  - Batch studies will be conducted after Task III
- Task V: TCE by-products and characterization of Fe°
  - This part will be conducted after Task IV

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