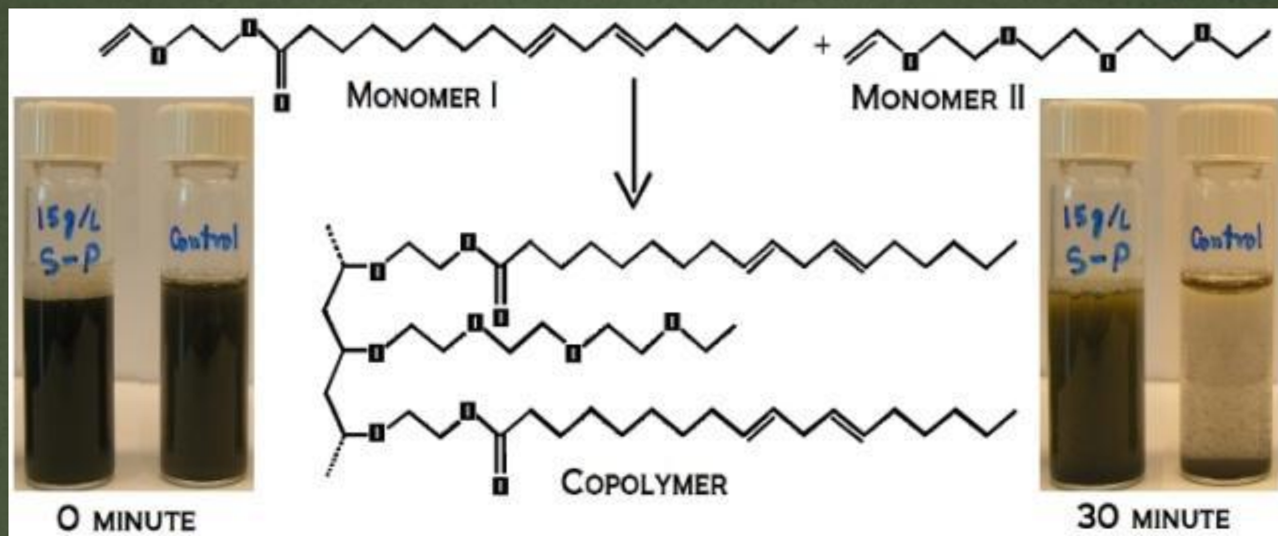
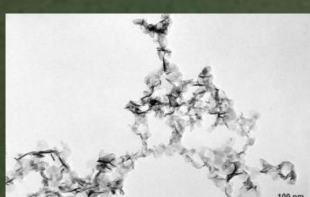
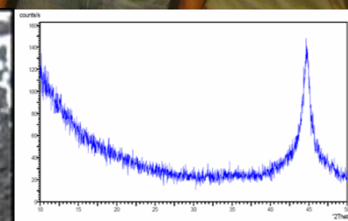
ECS Green Bag Lunch Presentation
by
Achintya Bezbaruah





October 5, 2010
12:30-1:30PM
Hidatsa, NDSU

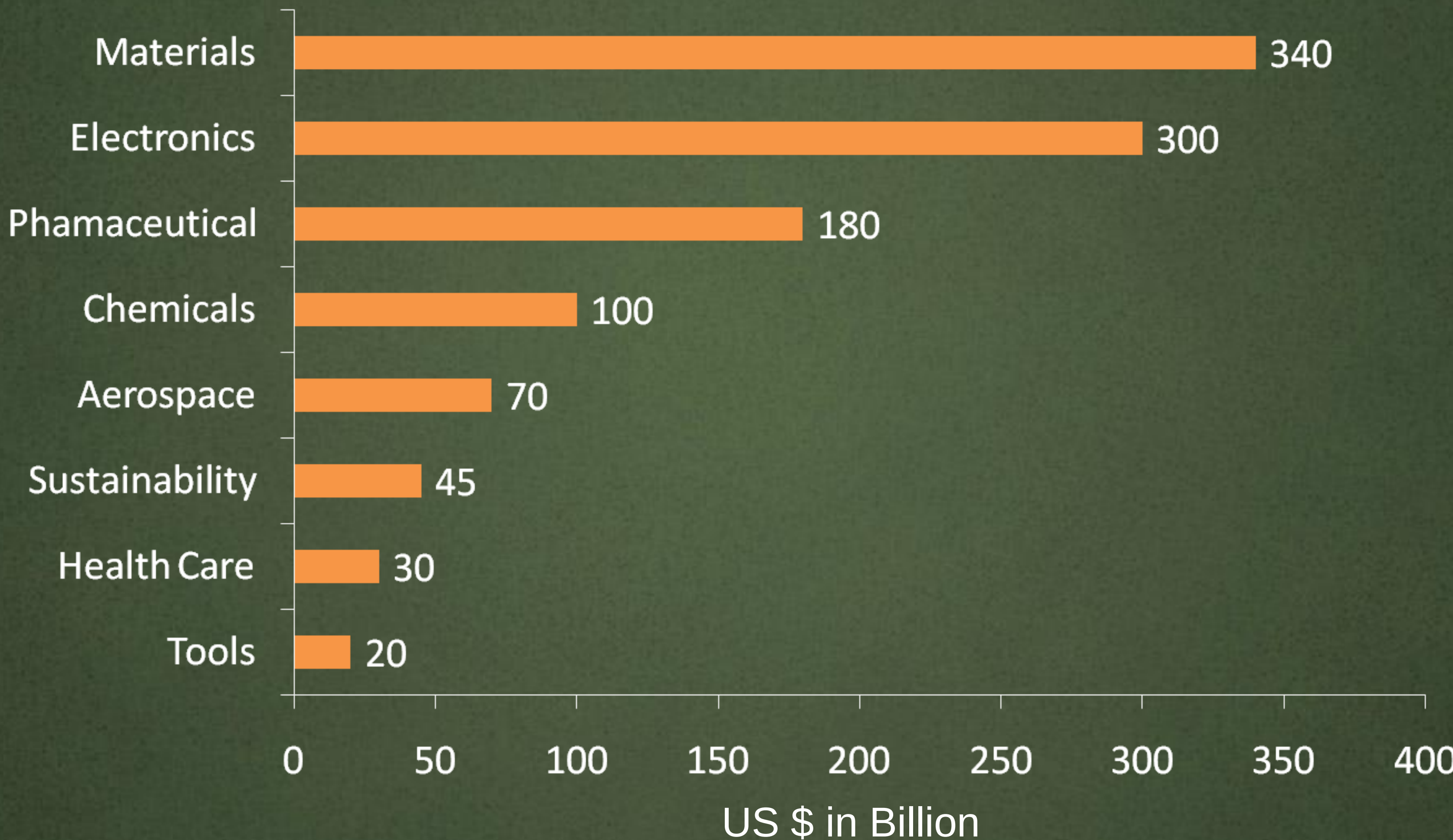


NRG Presents

A Brief Overview of

Nanoenvirology Research at NDSU

2015 World Nano Market



Source: NSF

Background: Iron Remediation

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

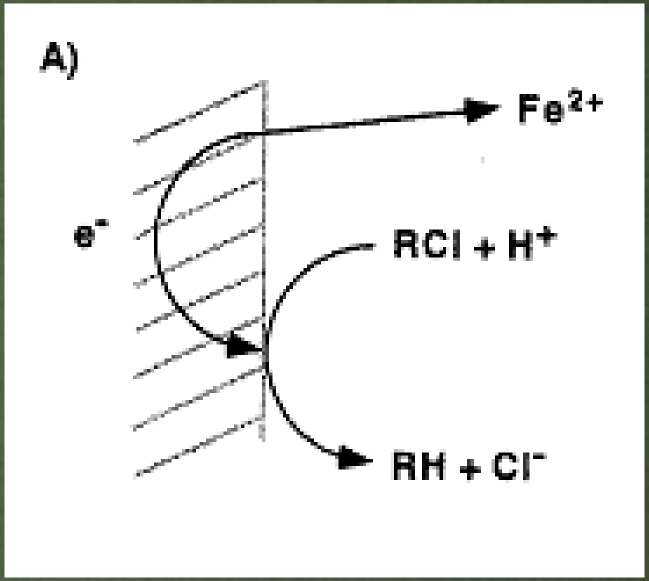


Image Credit: Matheson, L.J., Tratnyek, P.G., 1994. Environ. Sci. Technol. 28, 2045-2053.

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:

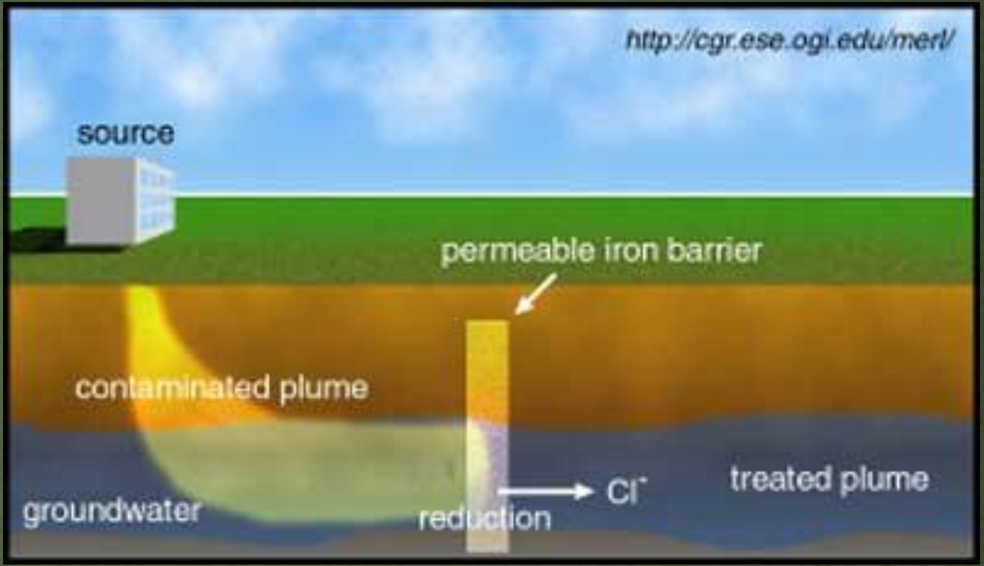
  $2Fe^{0} + O_2 + 2H_2O \leftrightarrow Fe^{2+} + 4OH^{-}$

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

Background: Iron Filings

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

- Successfully implemented in the field as permeable reactive barriers



Background: Nano-ZVI (NZVI)

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

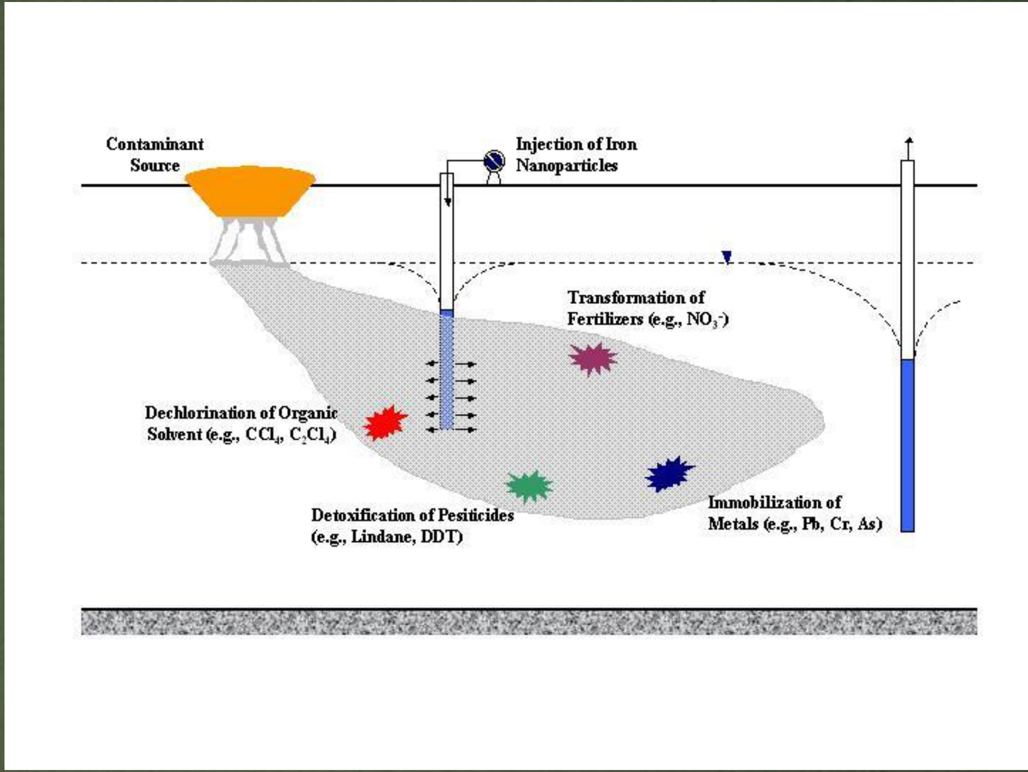


Image Credit: Zhang, W-X., 2003. J. Nanopart. Res. 5, 323-332.

NZVI: Reaction Speed

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

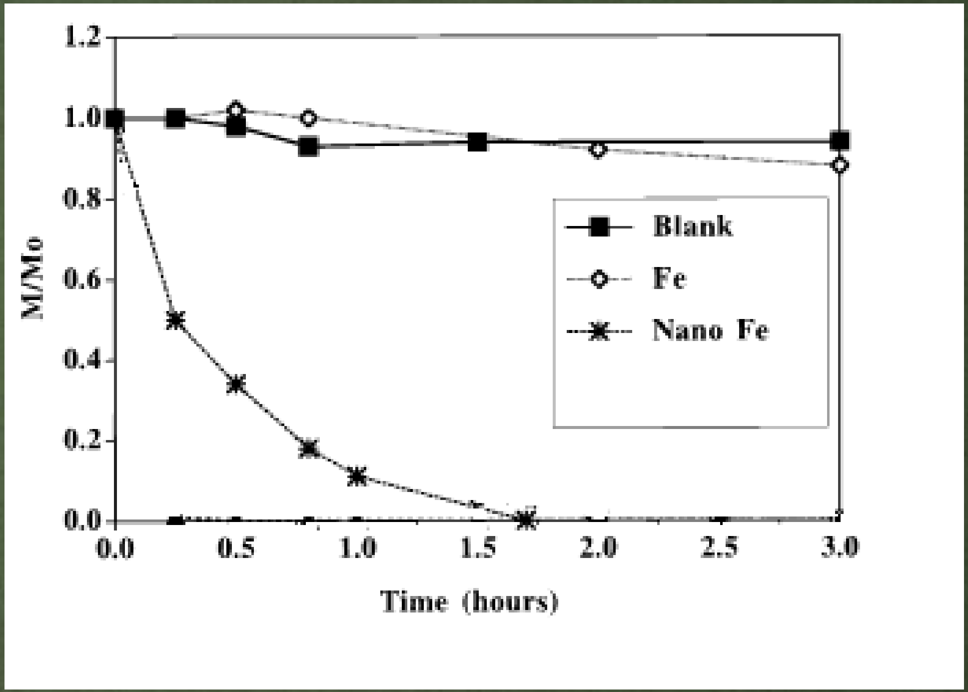


Image Credit: Wang, C.B., Zhang, W.X., 1997. Environ. Sci. Technol. 31, 2154-2156.

NZVI: Economics

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

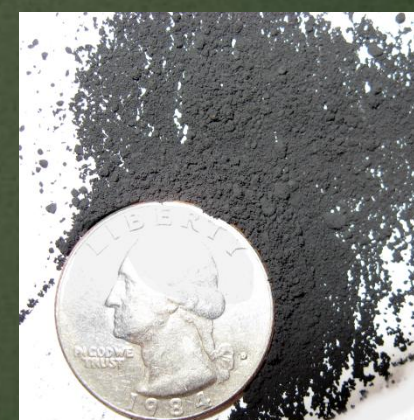
Image Credit :http://www.science.uwaterloo.ca

NZVI Synthesis

- Synthesis method: borohydride reduction

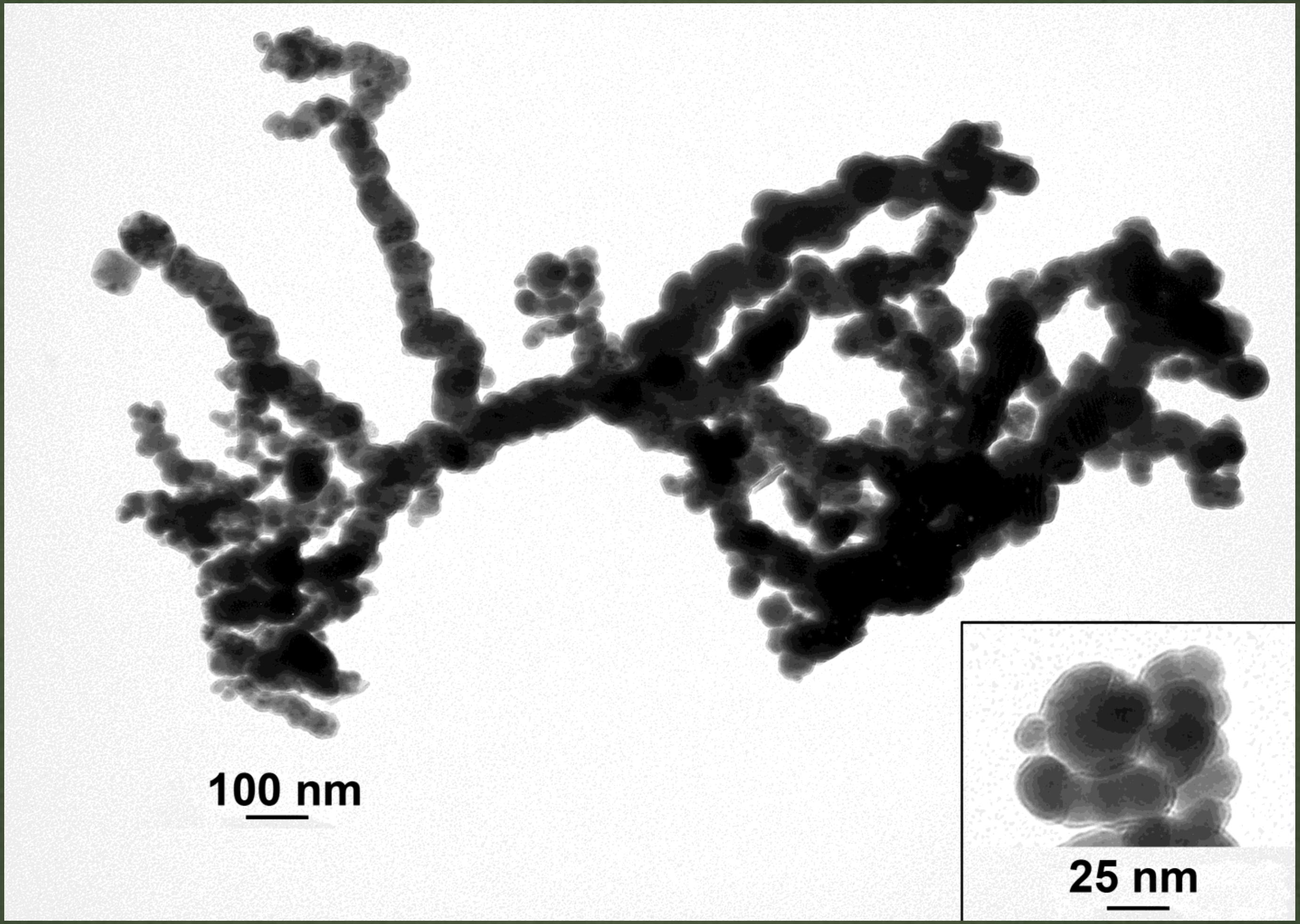
$$2Fe^{2+} + BH^{4-} + 3H_2O \rightarrow 2Fe^{0}\downarrow + H_2BO^{3-} + 4H^{+} + 2H_2$$

- Method is safe, inexpensive and well-studied

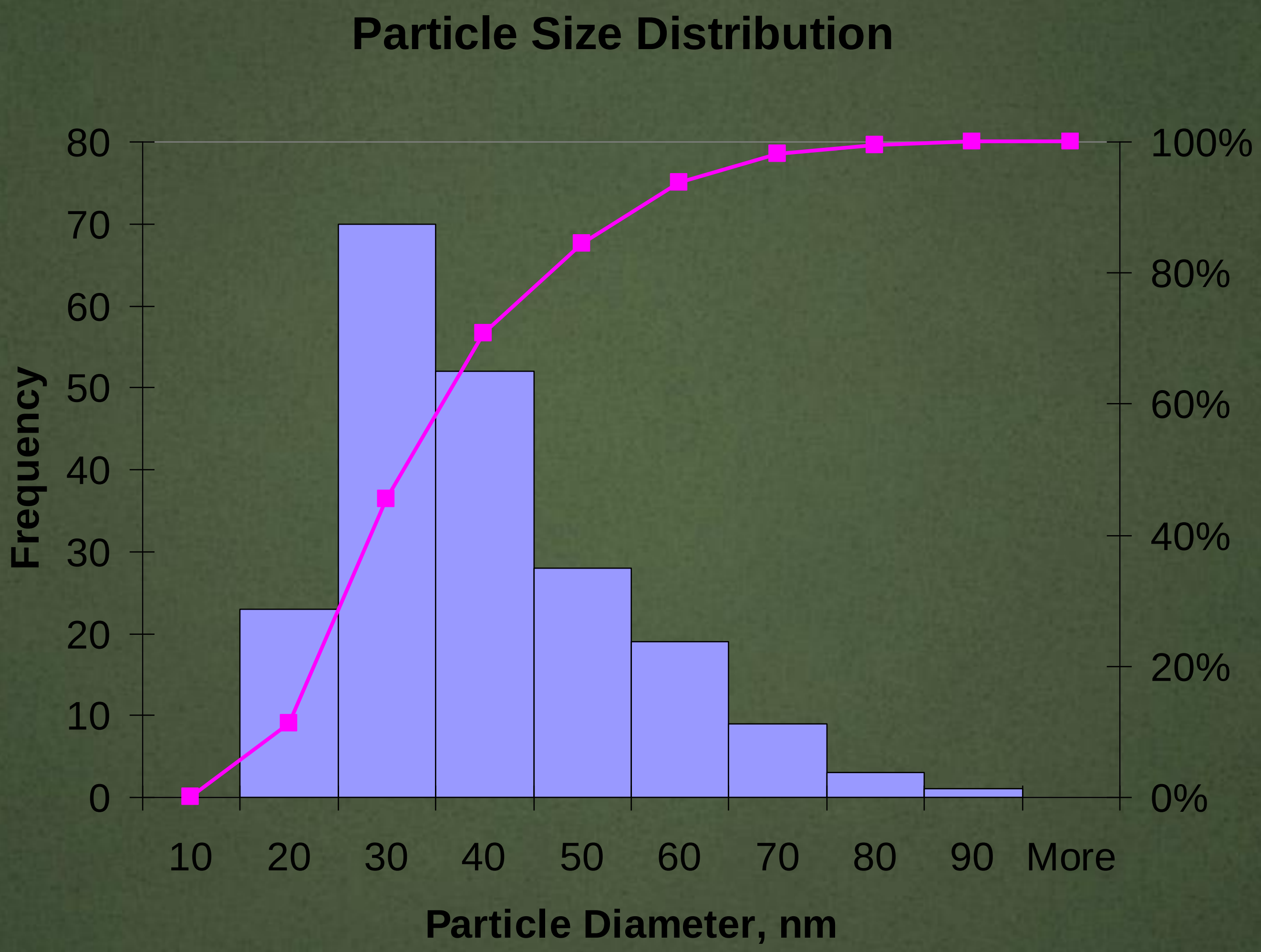


[1] Liu et al., *Environ. Sci. Technol.*, 2005; **[2]** Bezbaruah et al., *J. Haz. Mat.*, 2009

NZVI Characterization



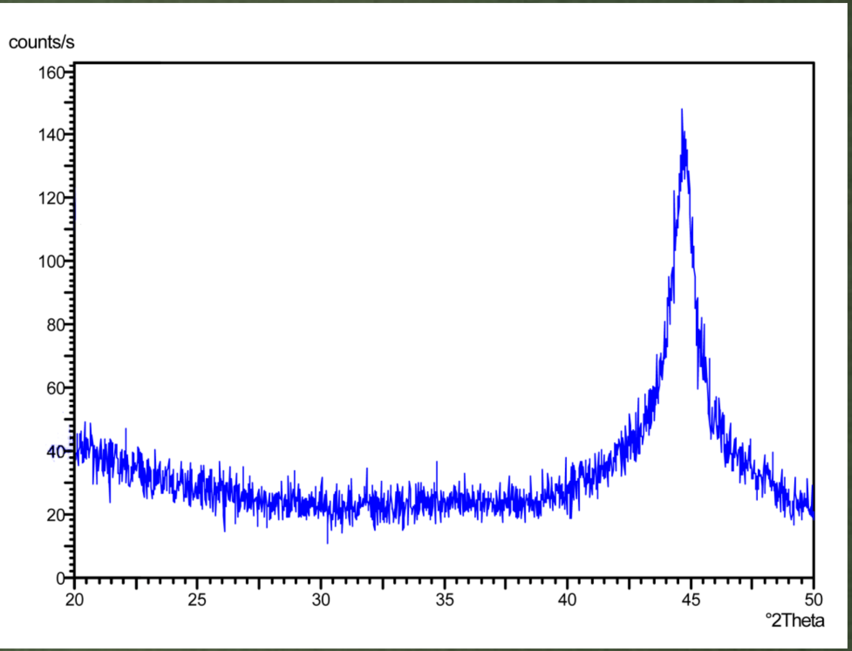
NZVI Characterization



NZVI 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



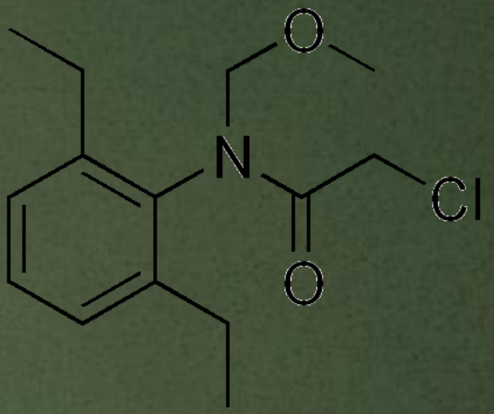
NZVI Characterization: Summary

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

Bare NZVI for Pesticide Removal

Reductive Degradation of Alachlor

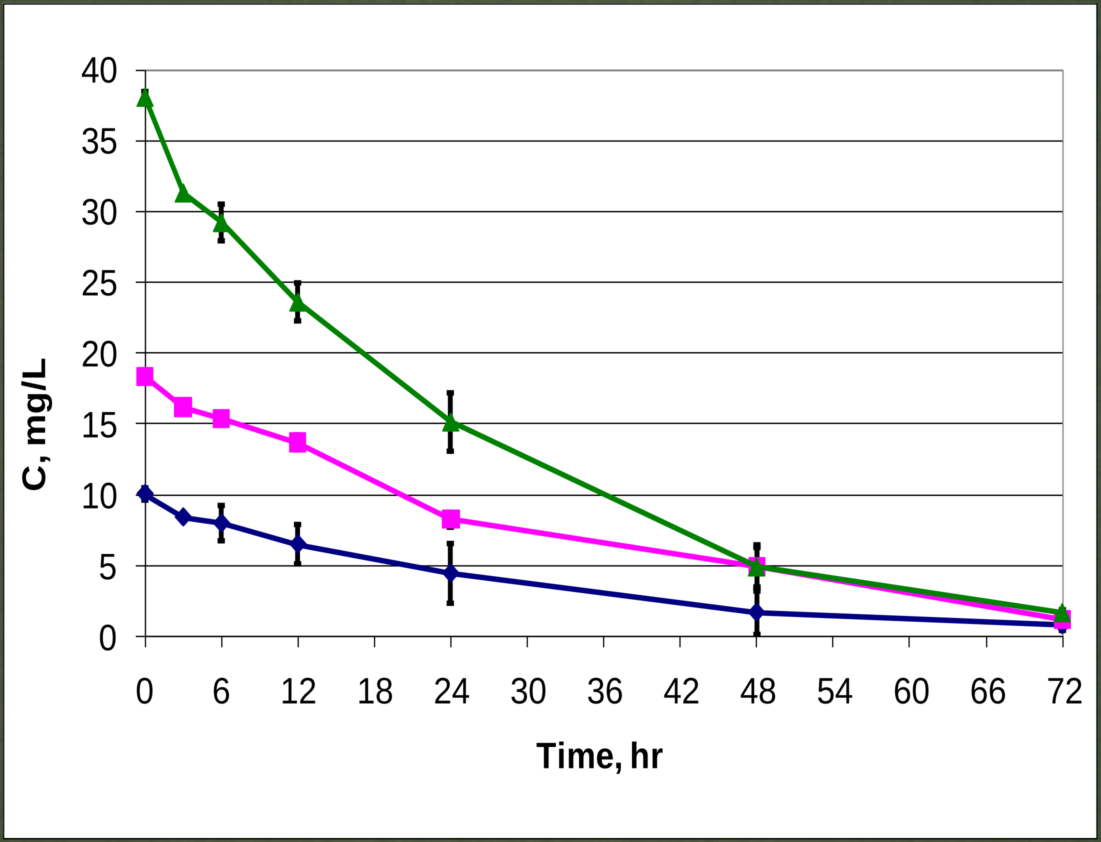
Funding: NDWRRI



- Herbicide for the control of grasses/weeds in corn and soybeans
- Maximum Contaminant Level (MCL) = 2 µg/L

Jay Thompson, MS

Results: Alachlor Kinetics



Bare NZVI for Phosphate Removal

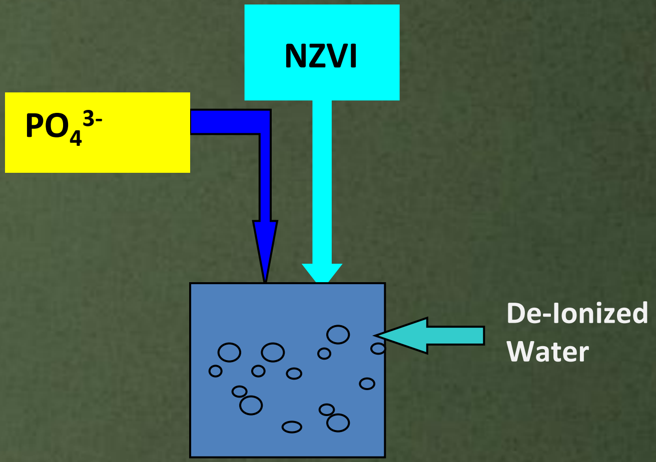
NZVI Slurry for Aqueous Phosphate Removal

Funding: Saudi Arabian Cultural Mission and NDSU-CE

Matthew Haugstad, BS

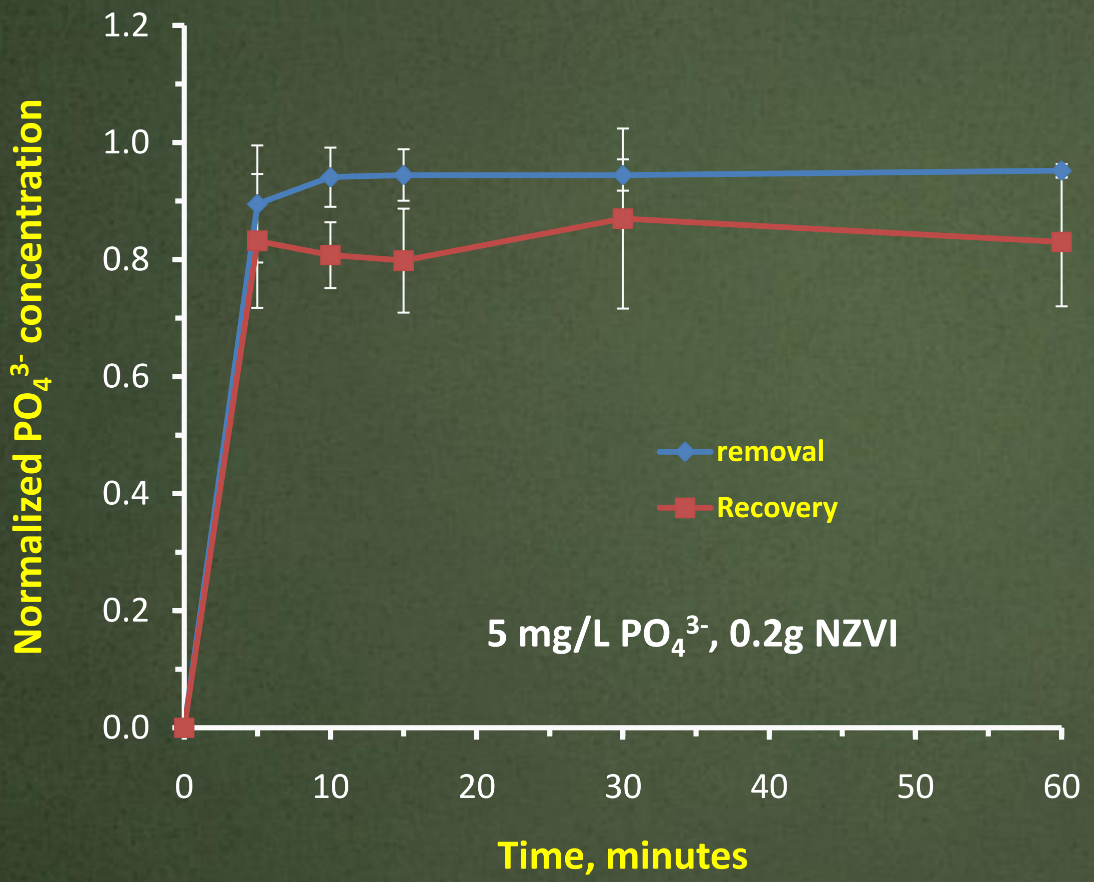
Talal Almeelbi, Ph.D

NZVI for Phosphate Removal



NZVI slurry/particles

NZVI Slurry for Aqueous Phosphate Removal



- Similar results with 1 mg/L and 10 mg/L of PO_4^{3-}
- At higher pH desorption is higher

Future Work: Phosphate Removal

- Compare NZVI efficiency with micro-ZVI and iron oxide nanoparticles.
- Study the effect of various parameter such as:
  - pH
  - redox conditions
  - ionic strength
  - presence of different ions

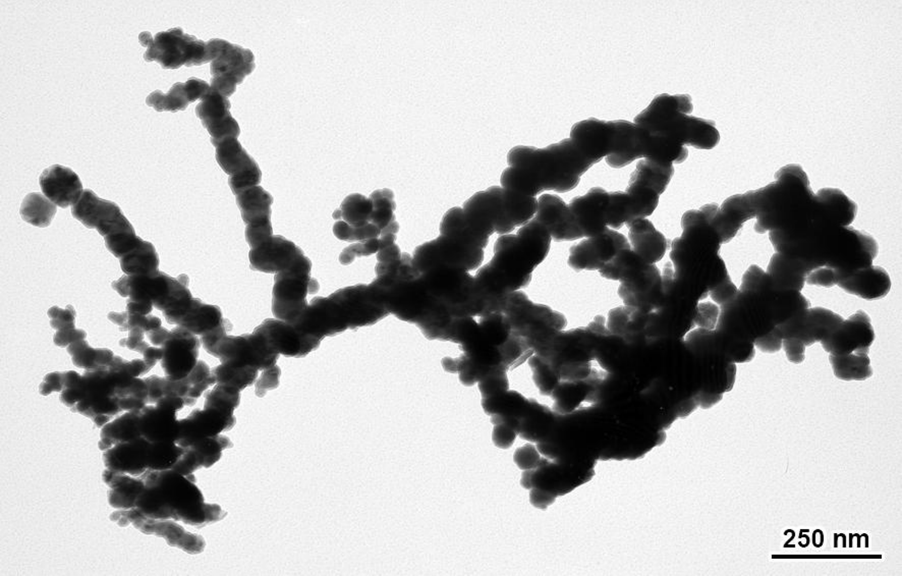
Entrapped NZVI for Arsenic Removal

Entrapped NZVI for Arsenic Removal

Funding: NDSU-CE

Objective: Entrapment of NZVI in alginate beads for effective treatment of arsenic contaminated groundwater

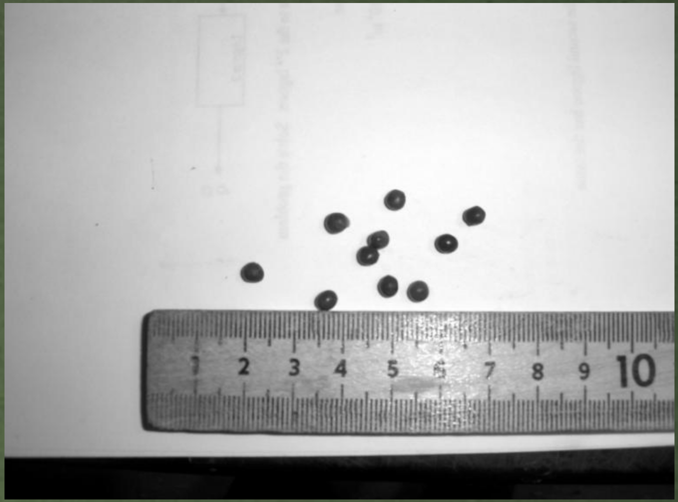
Chris Capecchi, BS



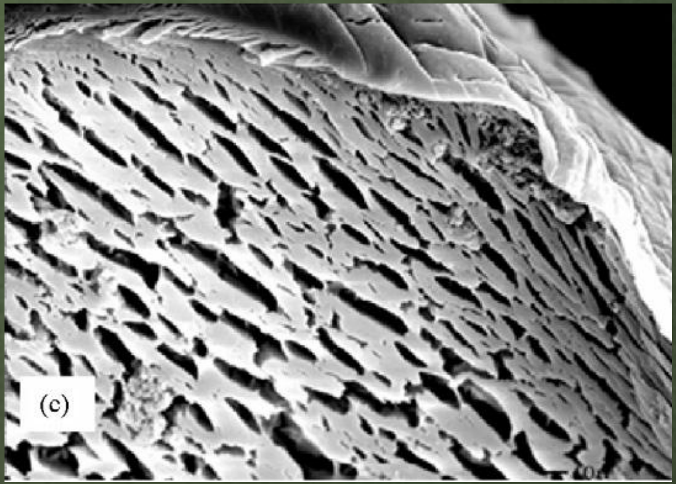
Bezbaruah et al., *J. Hazard. Mater.*, 2009

Why Alginate?

- Calcium alginate polymer is used as entrapment matrix
- Non-soluble in water
- Non-toxic
- Reduces particle agglomeration
- Biodegradable

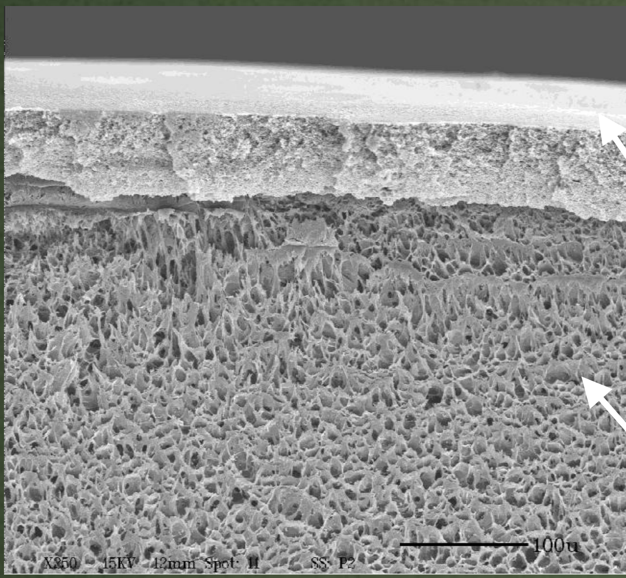


Alginate entrapped NZVI



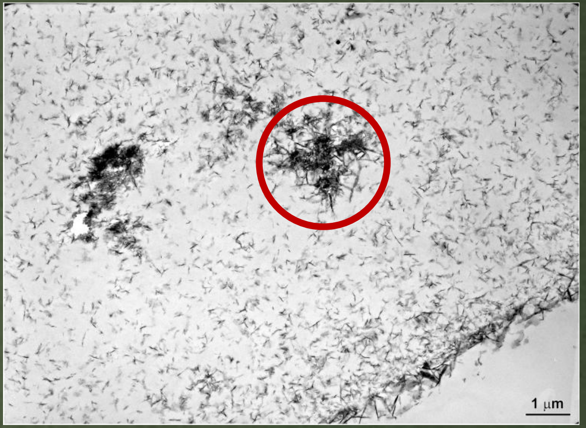
SEM image of NZVI-alginate bead

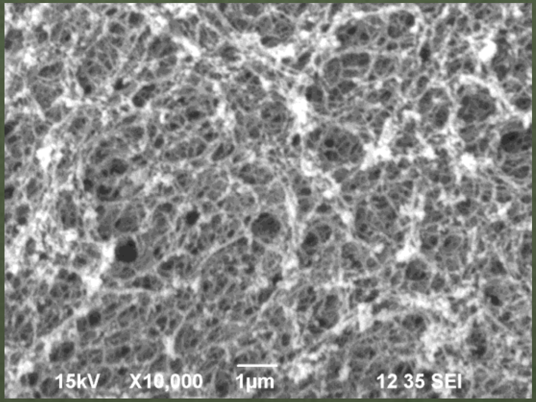
Looking into an Alginate Beads



Dense exterior layer

Porous interior layer

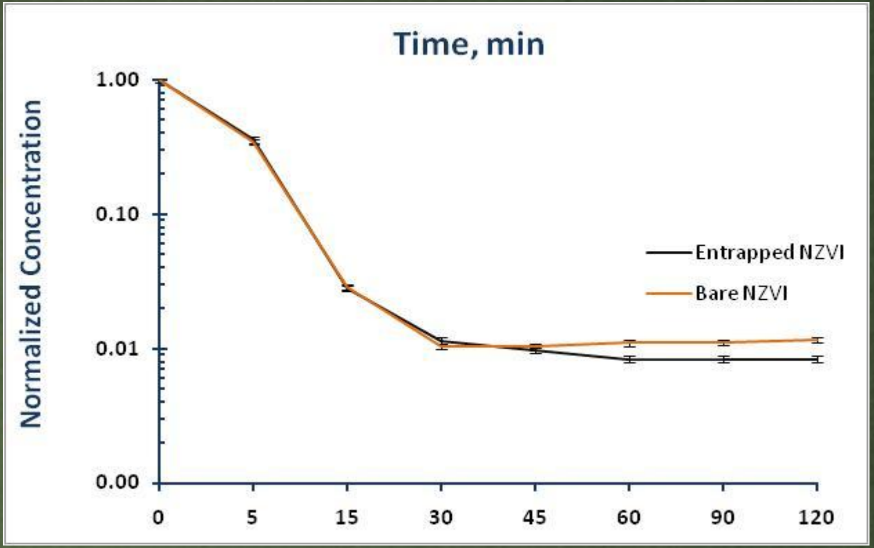


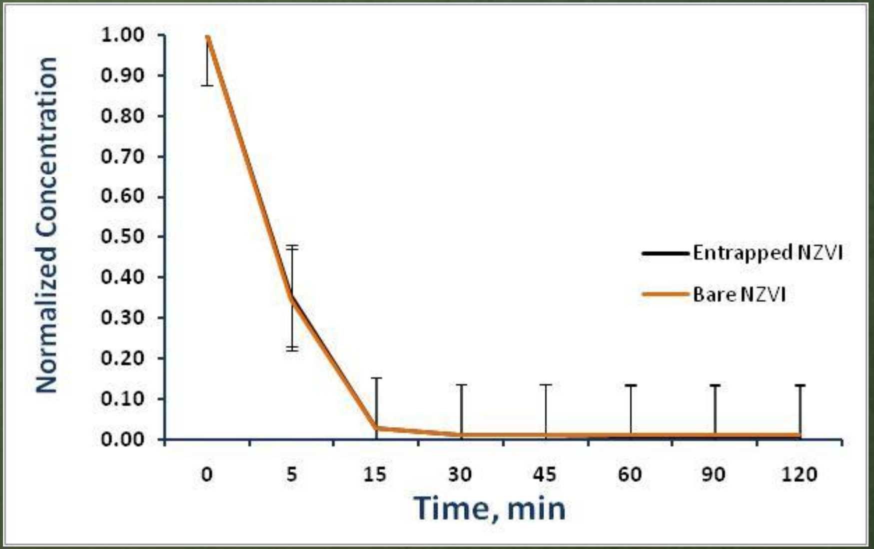


Arsenic: Results

Arsenic (IV) Batch Studies:

- After 45-60 minutes entrapped NZVI out performs bare NZVI
- Blank and control show negligible concentration change
- Entrapped beads can be used in PRB's





Future Work: Arsenic Removal

- Interference studies
- Area groundwater batch tests
- Arsenic (III) tests
- SEM / XRD analyses

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Development of APGC Delivery Vehicle

Graft Copolymer Coated NZVI

Funding: NDWRRI

Chad Mayfield, BS

Juan Elorza, BS

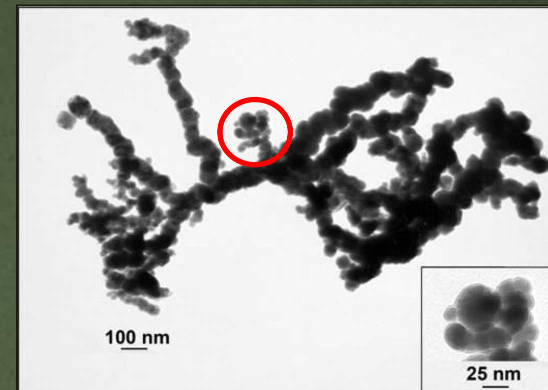
Sita Krajangpan, Ph.D

Mike Quamme, BS

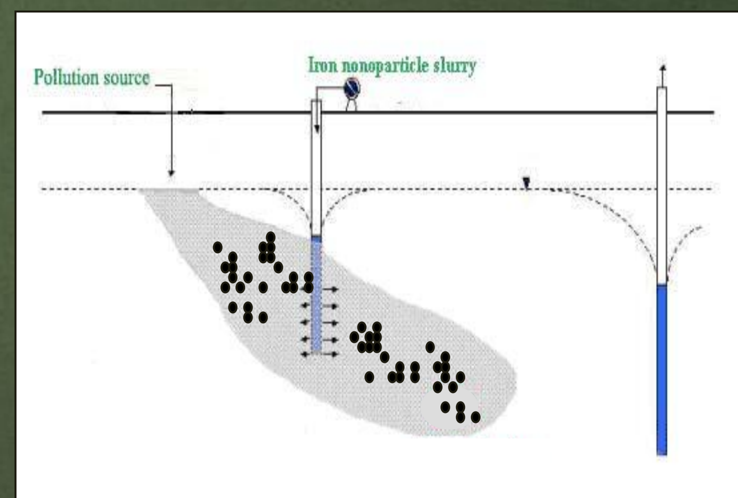
Amphiphilic Polysiloxane Graft Copolymer (APGC)

Objective: To modify nanoscale zero-valent iron (NZVI) particle surface using APGC for effective groundwater remediation

Hypothesis: APGC provide the colloidal stability and improve capabilities to NZVI for groundwater contaminant removal



Bezbaruah et al., *J. Hazard. Mater.*,**2009**, 166, 1339-1343.

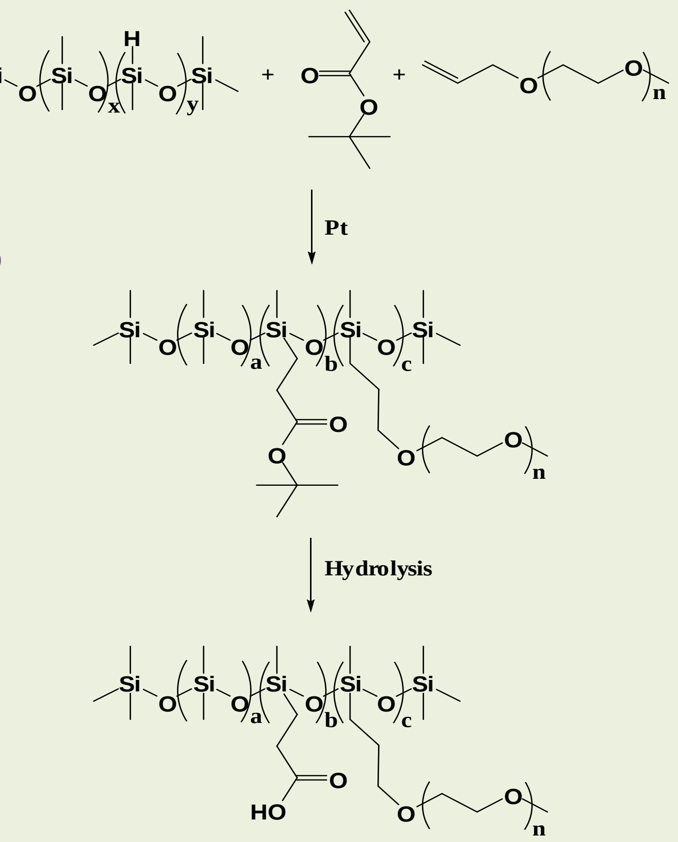


Oxidation rate↑, Dispersibility ↓, and Reactive surface area ↓

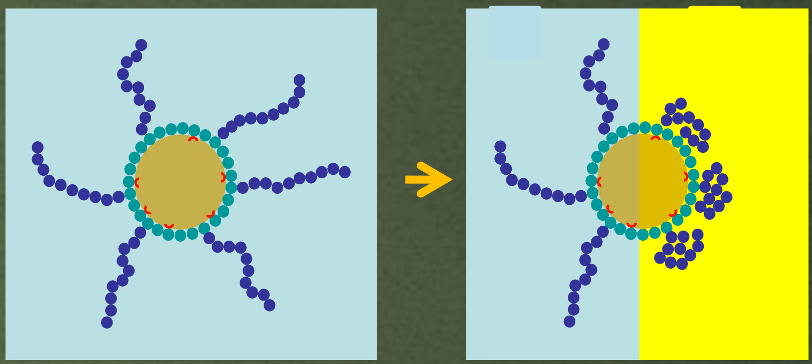
Our Design

APGC synthesis

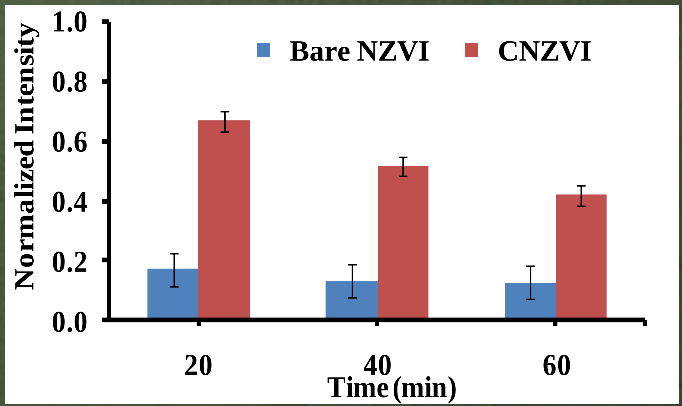
US Patent Pending



A schematic representation of APGC coated NZVI (CNZVI)



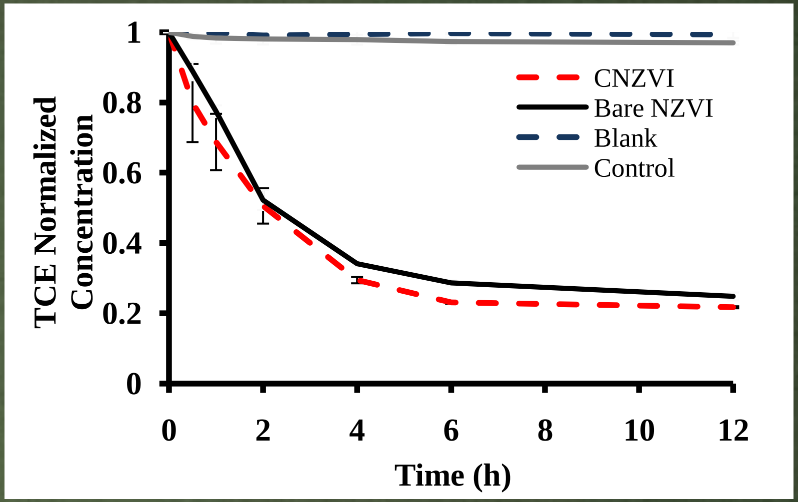
CNZVI has significantly higher colloidal stability than bare NZVI



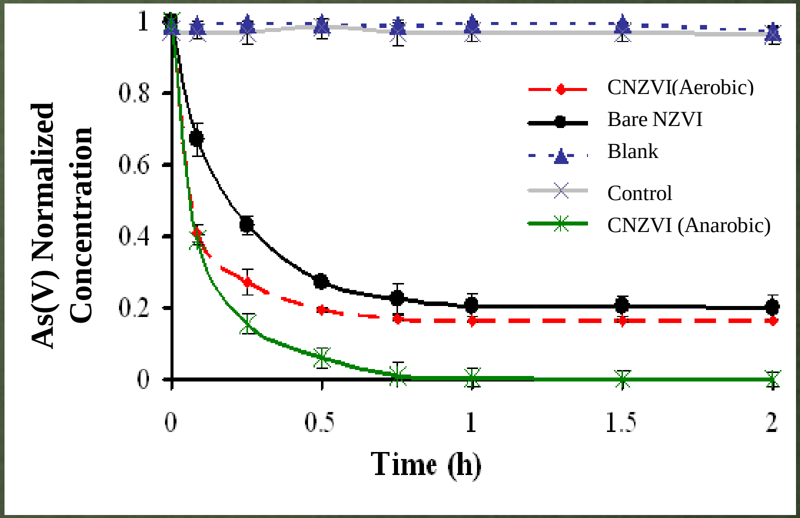
Krajangpan et al., American Society for Civil Engineers, **2009,** pp 191-212.
Krajangpan et al., *Polymer Preprint*, **2008**, 49, 921-922.

TCE and Arsenic Removal by CNZVI

- Initial concentrations of TCE and As(V): 1, 15, and 30 mg/L
- TCE batch study: 1.5 g/L of NZVI and CNZVI
- As(V) batch study: 1 g/L of NZVI and CNZVI
- Controls and blanks were ran simultaneously
- Aliquots withdrawn at definite time intervals
- TCE and As(V) were analyzed using GC-MS and ICP-AES



TCE kinetic study



As(V) kinetic study

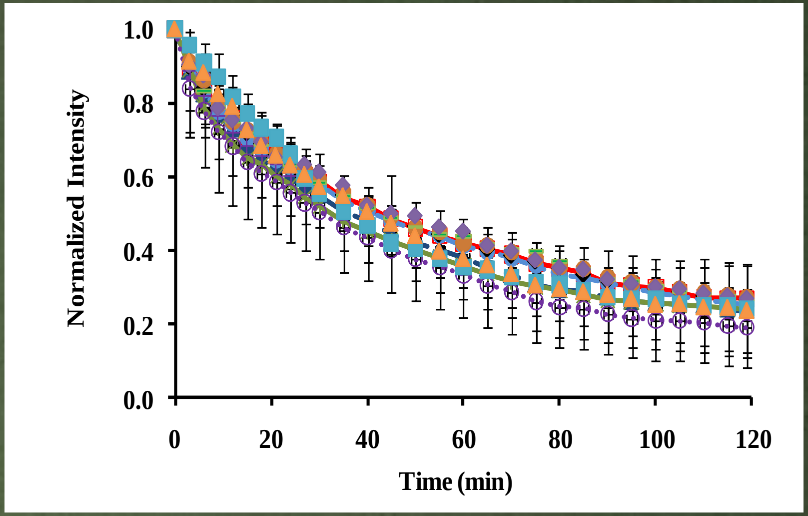
Shelf-life Studies

Sedimentation studies:

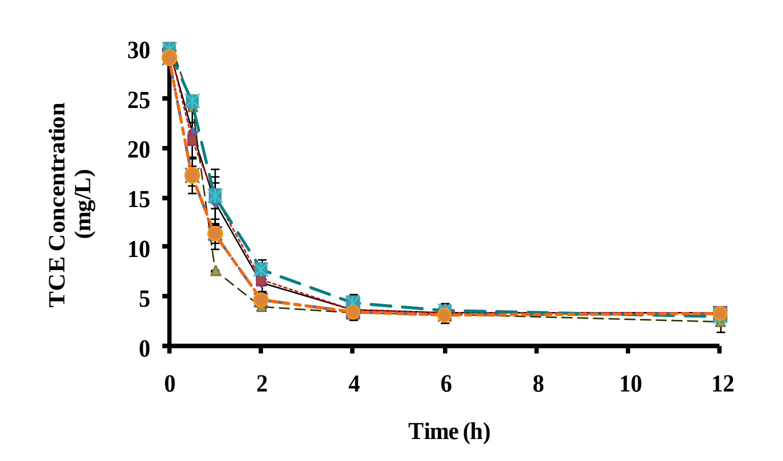
- Batch studies: 3 g/L of NZVI and 15 g/L of APGC
- 30 min sonication and 72 hr of 28 rpm rotation
- UV-VIS spectrophotometer

TCE kinetic studies:

- 1.5 g/L of NZVI and CNZVI
- 30 mg/L of TCE initial concentration
- TCE was analyzed using GC-MS



CNZVI sedimentation studies:12 month-period



CNZVI-TCE kinetic studies: 6 month-period

Biodegradation of APGC

APGC Biodegradation

Funding: NDWRRI & ECS Program

Dhritikshama Roy, Ph.D

PDMS Biodegradation

Viability test for microorganisms

<u>Control</u> :
Microorganism
(from batch study)
+ media

PDMS + mineral
media + microbes

<u>Further research needed</u>

Microorganisms growing
on PDMS spread plates

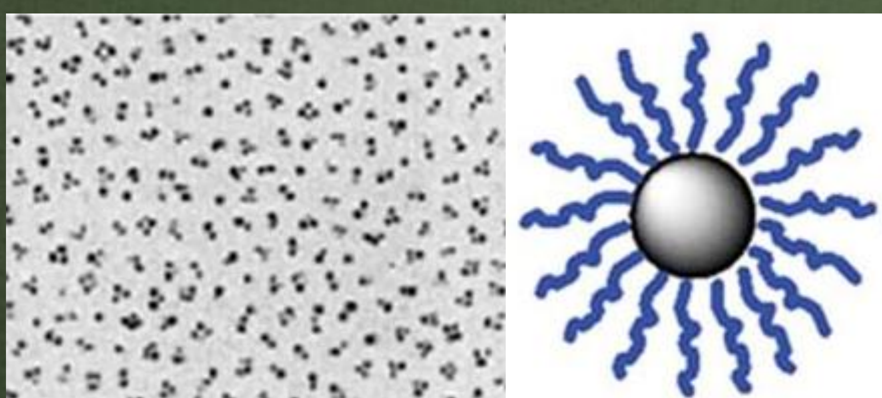
Biodegradable Polymers

Funding: NDWRRI & ND Soybean Council

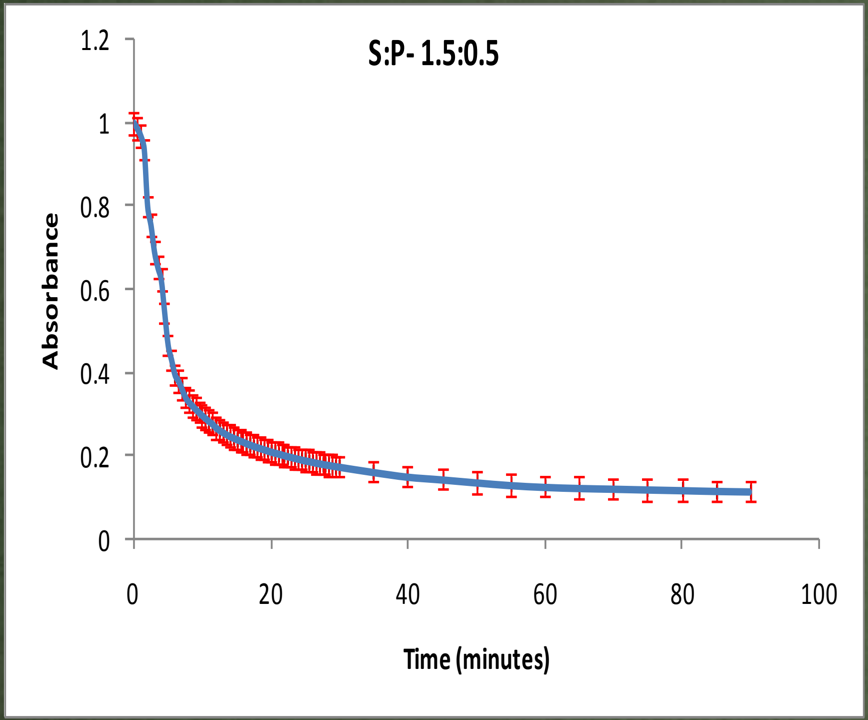
Objective: Synthesis of biodegradable amphiphilic copolymer from soybean oil

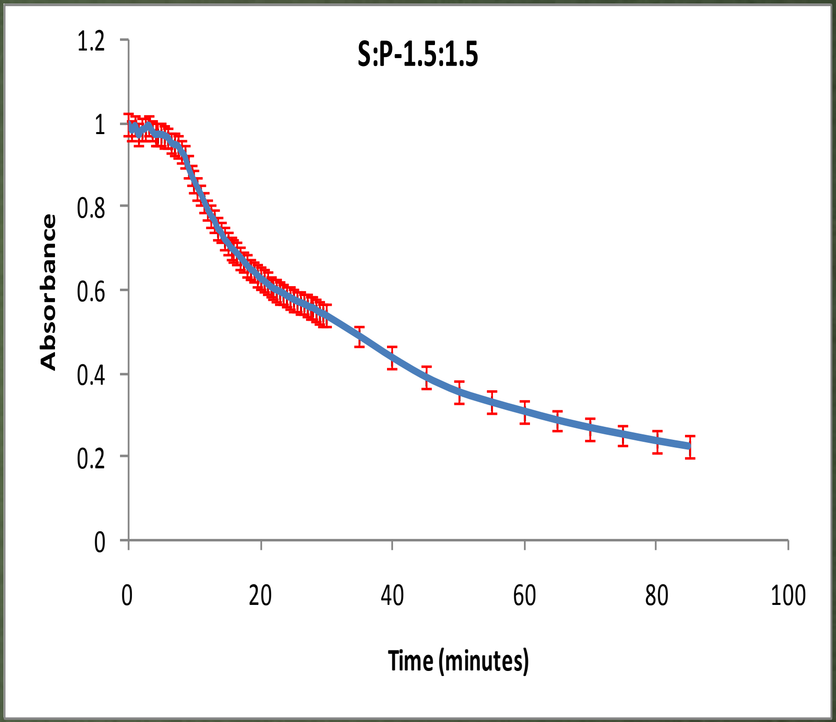
- Hypotheses: The copolymer will be biodegradable if synthesized with biodegradable soybean oil and PEG.

Harjyoti Kalita, Ph.D



Soy-based Co-Polymer: Sedimentation Studies





S:P (Soybean : PEG, wt%)

US Patent application to be filed

Micro-organism-NZVI Interactions

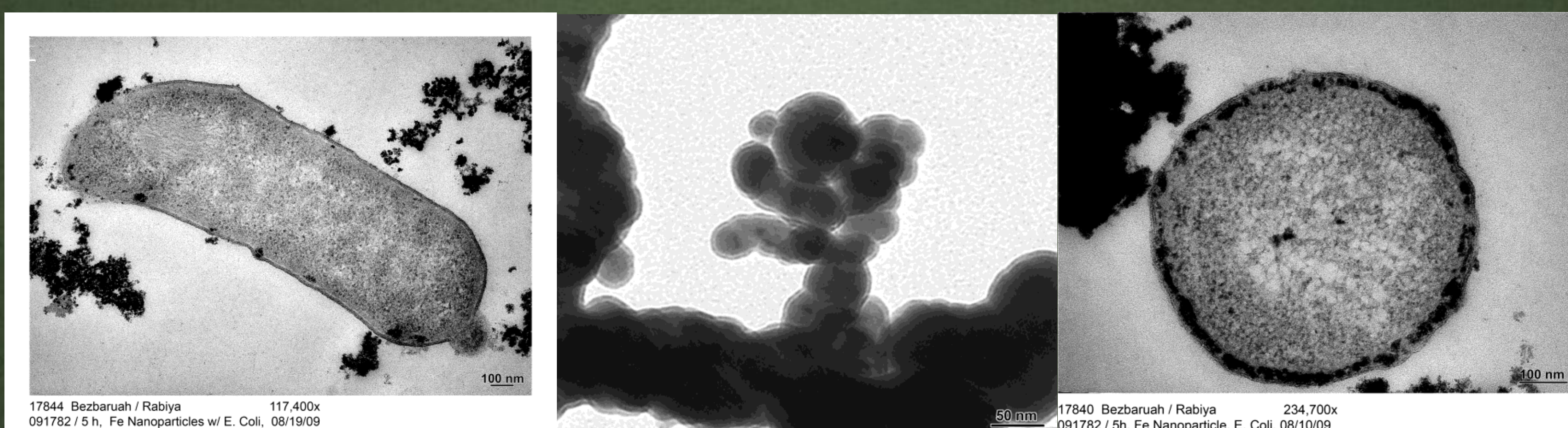
Iron Nanoparticle-Microorganism Interactions: Compatibility Studies

Funding : NDWRRI & ECS Program

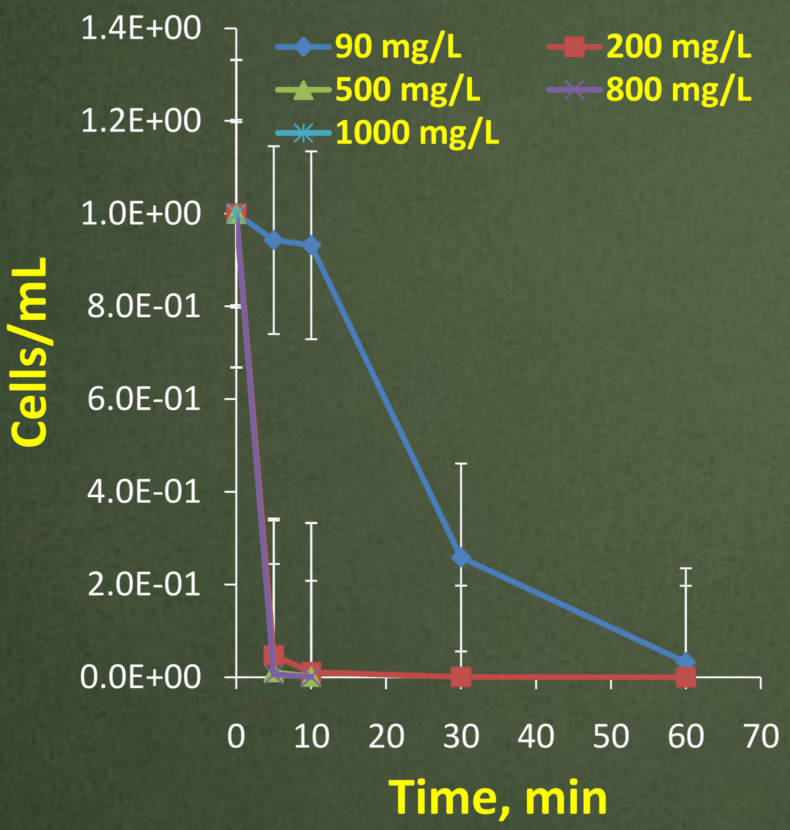
Objective: To understand microorganism-NZVI interactions

Hypothesis: Microorganisms can establish a “symbiotic relationship” with NZVI

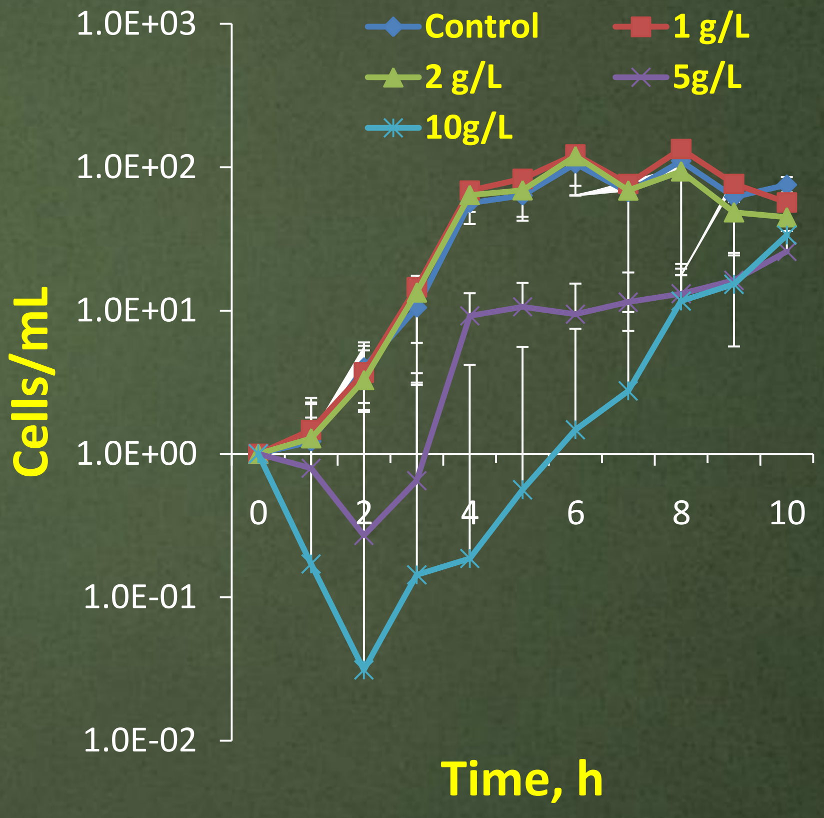
Rabiya Shabnam, MS



E. coli 8739-NZVI Interactions



In buffer solution

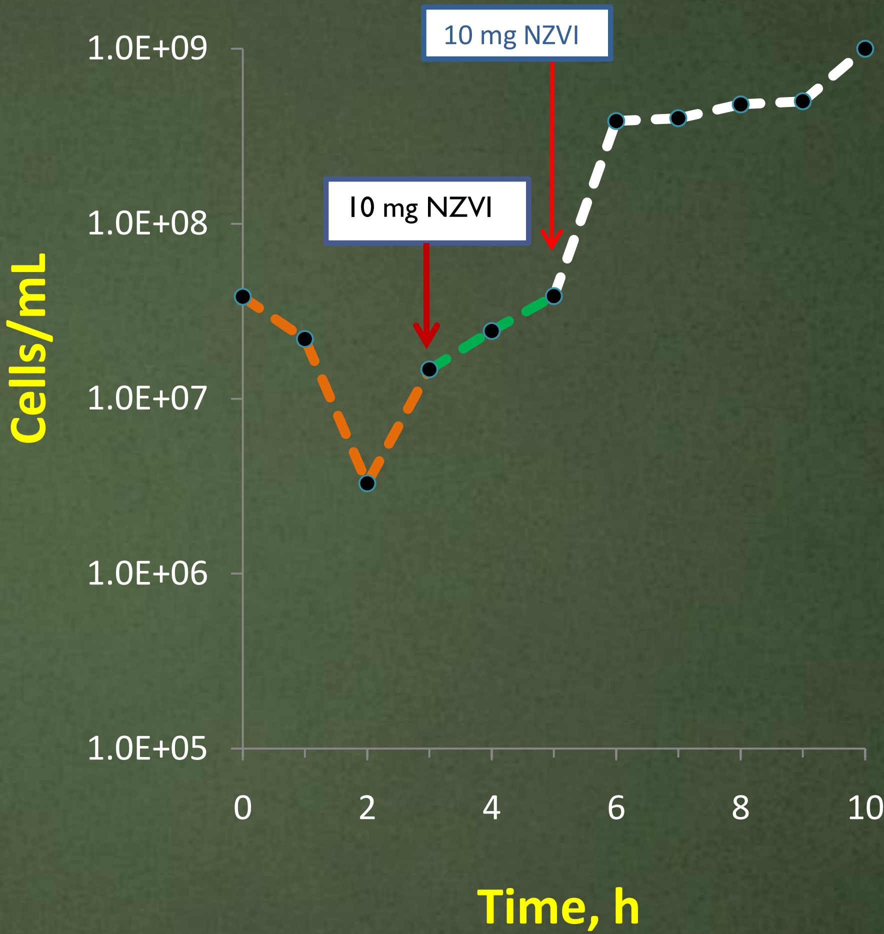


In growth media

Bacteria-NZVI Interactions

Findings:

- Bacteria in a lag or early exponential phase are affected by NZVI
- Actively growing bacteria are not effected by NZVI
- Non-replicating bacteria are more susceptible to NZVI toxicity



Microbial Studies: Summary

Findings: Bactericidal effects of NZVI depend on:

- NZVI concentration
- Physical condition of the cell membrane
- Growth phase of the bacteria
- *E. coli* 8739, Jm109 and *Pseudomonas putida* F1 show similar effects with NZVI

TEM micrograph of *E.coli* 8739 with NZVI (5h)

Encapsulated NZVI for TCE Removal

Co-entrapment of NZVI-microorganisms for Groundwater Remediation

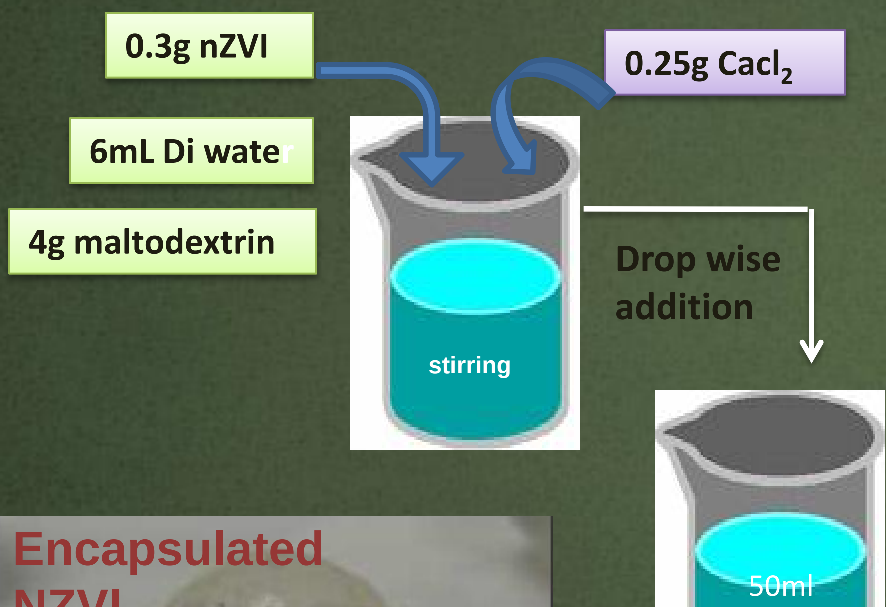
Funding: NDSU-CE

Objectives: NZVI and microorganism Co-entrapment in alginate beads for groundwater TCE degradation

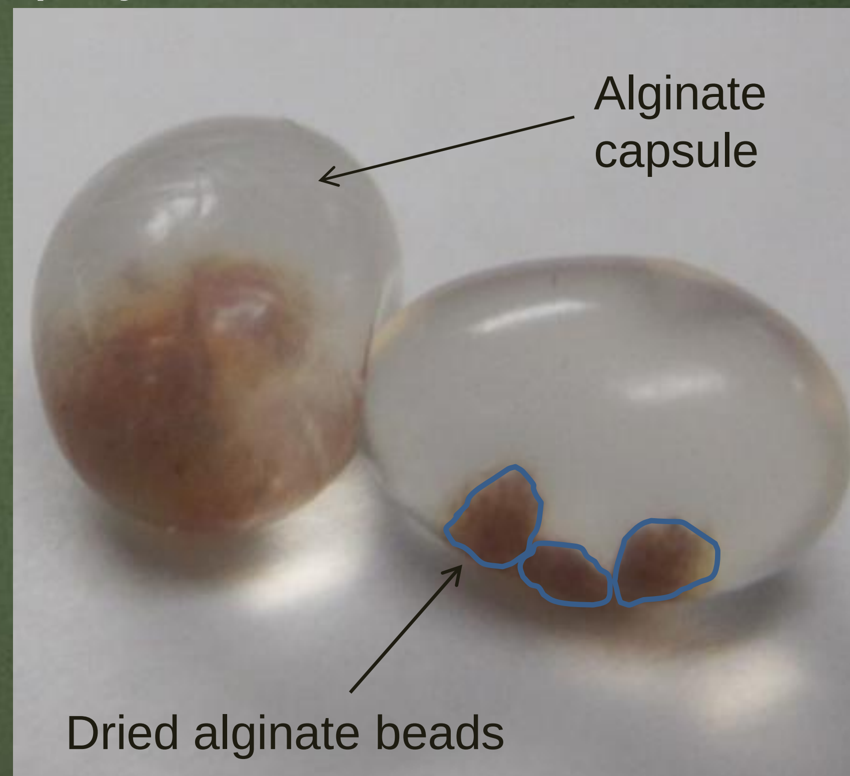
Shanaya Shanbhogue, MS

Milestones

Encapsulation of NZVI

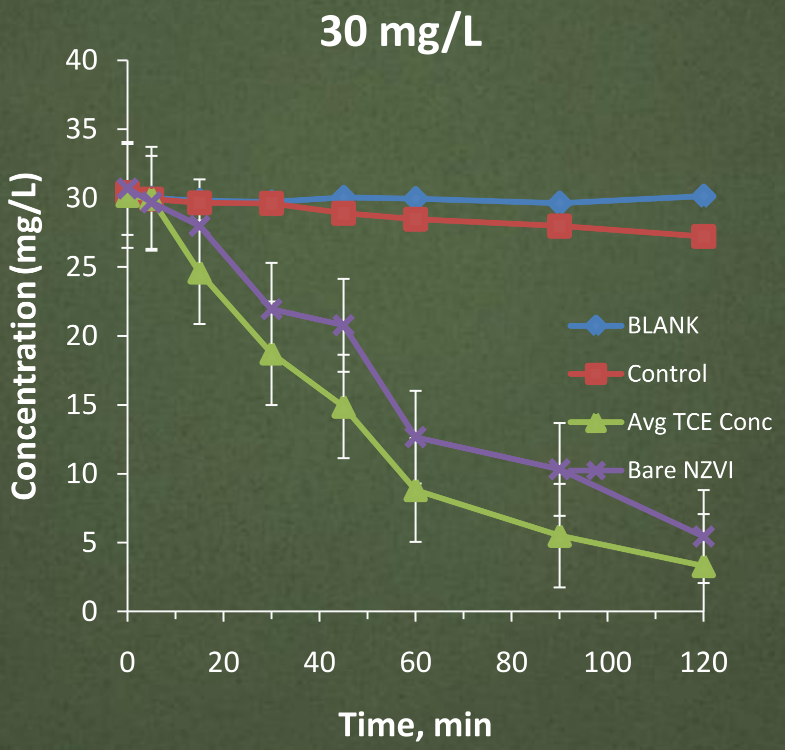


Encapsulation of Dried alginate beads in alginate polymer



TCE Degradation: Results

TCE degradation using Encapsulated NZVI



Patents/Publications

- Krajangpan, S., Chishlom, B., Bezbaruah, A. (2010) RFT-247 & RFT-247A, Novel Polymer Modified Iron Nanoparticles for Environmental Remediation, US patent. (Patent)
- Kalita, H, Chishlom, B., Bezbaruah, A. (2010), Soybean-based Copolymer, to be filled (Patent)
- Krajangpan, S., Jarabek, L., Jepperson, J., Chisholm, B., Bezbaruah, A. (2008). Polymer Modified Iron Nanoparticles for Environmental Remediation, *Polymer Preprint*, 49, 921-922.
- Bezbaruah, A.N., Krajangpan, S., Chisholm, B.J., Khan, E., Bermudez, J.J.E., (2009). Entrapment of Iron Nanoparticles in Calcium Alginate Beads for Groundwater Remediation Applications, *Journal of Hazardous Materials*, 166, 1339-1343.
- Krajangpan, S., Chisholm, B.J., Kalita, H., Bezbaruah, A.N. (2009). Challenges in Groundwater Remediation with Iron Nanoparticles: Enhancement Colloidal Stability (Chapter 8) in *Nanotechnologies for Water Environment Applications* (Eds: Zhang, T.C., Surampalli, R.Y., Lai, K.C.K., Hu, Z., Tyagi, R.D., Lo, I.M.C.), American Society for Civil Engineers, pp 191-212. (Book Chapter)
- Thompson, J.M., Chisholm, B.J., Bezbaruah, A.N. (2010). Reductive Dechlorination of Chloroacetanilide Herbicide (Alachlor) Using Zero-valent Iron Nanoparticles, *Environmental Engineering Science,* 27, 227-232.

Patents/Publications

- Kalita, H., Chisholm, B., Bezbaruah, A. (2009) Effects of different graft copolymer constituent groups on sedimentation characteristics of coated iron nanoparticles, *PSME Preprints,* 100:683-685**.**
- Bezbaruah, A.N. and Kalita, H. (2010) Sensors and Biosensors for Endocrine Disrupting Chemicals Stateofthe- art and Future Trends in *Treatment of Micropollutants in Water and Wastewater (Eds: Virkutyte,* J., Varma, R.S., Jegatheesan, V.), International Water Association, London,, U.K., ISBN: 9781843393160, pp.92-128. (Book Chapter)
- Bezbaruah, A.N., Thompson, J.M., Chisholm, B.J. (2009) Remediation of alachlor and atrazine contaminated water with zero-valent iron nanoparticles, *Journal of Environmental Science and Health Part BPesticides, Food Contaminants, and Agricultural Wastes,* 44:518-524.
- Thompson, J.M., Bezbaruah, A.N. *Selected Pesticide Remediation with Iron Nanoparticles: Modeling and Barrier Applications*. Technical Report No. ND08-04. North Dakota Water Resources Research Institute, Fargo, ND, 2008.

The Present Extended NanoTeam









Our Website

http://www.ndsu.edu/pubweb/~bezbarua/

Thank You!