ECS Green Bag Lunch Presentation
by
Achintya Bezbaruah

October 5, 2010
12:30-1:30PM
Hidatsa, NDSU
NRG Presents
A Brief Overview of Nanoenviroloogy Research at NDSU
2015 World Nano Market

<table>
<thead>
<tr>
<th>Sector</th>
<th>US $ in Billion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
<td>340</td>
</tr>
<tr>
<td>Electronics</td>
<td>300</td>
</tr>
<tr>
<td>Pharmaceutical</td>
<td>180</td>
</tr>
<tr>
<td>Chemicals</td>
<td>100</td>
</tr>
<tr>
<td>Aerospace</td>
<td>70</td>
</tr>
<tr>
<td>Sustainability</td>
<td>45</td>
</tr>
<tr>
<td>Health Care</td>
<td>30</td>
</tr>
<tr>
<td>Tools</td>
<td>20</td>
</tr>
</tbody>
</table>

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

Background: Iron Redox

• Redox Reactions:
  \[ \text{Fe}^{2+} + 2e^- \leftrightarrow \text{Fe}^0 \quad -0.440 \text{ V} \]
  \[ \text{Fe}^0 + RX + H^+ \rightarrow \text{Fe}^{2+} + RH + X^- \]

• Competing Reactions:
  \[ 2\text{Fe}^0 + O_2 + 2\text{H}_2\text{O} \leftrightarrow \text{Fe}^{2+} + 4\text{OH}^- \]
  \[ \text{Fe}^0 + 2\text{H}_2\text{O} \leftrightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- \]
• 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

NZVI: Reaction Speed

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

NZVI: Economics

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

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

• Synthesis method: borohydride reduction

\[ 2\text{Fe}^{2+} + \text{BH}_4^- + 3\text{H}_2\text{O} \rightarrow 2\text{Fe}_0\downarrow + \text{H}_2\text{BO}_3^- + 4\text{H}^+ + 2\text{H}_2 \]

• Method is safe, inexpensive and well-studied

NZVI Characterization
NZVI Characterization

Particle Size Distribution

Particle Diameter, nm

Frequency

0%
20%
40%
60%
80%
100%

More
• XRD detects no iron oxides (typical corrosion products are hematite and magnetite)

• BET surface area analysis determined specific surface area to be 26 m²/g
## NZVI Characterization: Summary

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Reported Values (NZVI, BH only)</th>
<th>Our Observed Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Particle Size (nm)</td>
<td>20-70</td>
<td>35</td>
</tr>
<tr>
<td>BET Surface Area (m²/g)</td>
<td>20-55</td>
<td>26</td>
</tr>
<tr>
<td>Shell Thickness (nm)</td>
<td>2-3</td>
<td>~2.5</td>
</tr>
</tbody>
</table>
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 $\text{PO}_4^{3-}$
- At higher pH desorption is higher

5 mg/L $\text{PO}_4^{3-}$, 0.2g NZVI

Normalized $\text{PO}_4^{3-}$ concentration

Time, minutes
Future Work: Phosphate Removal

• Compare NZVI efficiency with micro-ZVI and iron oxide nanoparticles.
• Study the effect of various parameter such as:
  o pH
  o redox conditions
  o ionic strength
  o 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
Looking into an Alginate Beads

Dense exterior layer

Porous interior layer
Arsenic (IV) Batch Studies:

- After 45-60 minutes entrapped NZVI outperforms 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
Development of APGC Delivery Vehicle
Graft Copolymer Coated NZVI

Funding: NDWRRI

Sita Krajangpan, Ph.D

Chad Mayfield, BS

Juan Elorza, BS

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


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

APGC synthesis

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.
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
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
Biodegradation of APGC
APGC Biodegradation

Funding: NDWRRI & ECS Program

Dhritikshama Roy, Ph.D
PDMS Biodegradation

Viability test for microorganisms

Control: Microorganism (from batch study) + media

PDMS + mineral media + microbes

Further research needed

Microorganisms growing on PDMS spread plates
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.

Harjyot Kalita, Ph.D
Soy-based Co-Polymer: Sedimentation Studies

S:P (Soybean : PEG, wt%)
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
Findings:

• Bacteria in a lag or early exponential phase are affected by NZVI

• Actively growing bacteria are not affected by NZVI

• Non-replicating bacteria are more susceptible to NZVI toxicity
**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-entrainment in alginate beads for groundwater TCE degradation

Shanaya Shanbhogue, MS
Encapsulation of NZVI

Encapsulation of Dried alginate beads in alginate polymer

- 0.3g nZVI
- 0.25g CaCl₂
- 6mL Di water
- 4g maltodextrin

Drop wise addition

Alginate capsule

Encapsulated NZVI

50ml 1% alginate

Dried alginate beads

Nanoparticles

NZVI
TCE Degradation: Results

TCE degradation using Encapsulated NZVI

![Graph showing TCE degradation using Encapsulated NZVI with time and concentration on the axes.]

Kalita, H, Chishlom, B., Bezbaruah, A. (2010), Soybean-based Copolymer, to be filled (Patent)


The Present Extended NanoTeam
Our Website
http://www.ndsu.edu/pubweb/~bezbarua/

Thank You!