Emerging Opportunities of Nanotechnology to Address Groundwater Remediation Challenges and Enhance Bioremediation

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Nano = Dwarf (Greek) = $10^{-9}$

“Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications.”

-National Nanotechnology Initiative
## Opportunities for Engineered Nanomaterials (ENMs) in Hazardous Waste Treatment (mainly above-ground applications)

<table>
<thead>
<tr>
<th><strong>ENM Properties</strong></th>
<th><strong>Examples of Enabled Technologies</strong></th>
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<tbody>
<tr>
<td>Large surface area to volume ratio</td>
<td>Superior sorbents (e.g., nanomagnetite or graphene oxides to remove heavy metals and radionuclides)</td>
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<td>Enhanced catalytic properties</td>
<td>Hypercatalysts for advanced oxidation &amp; reduction processes</td>
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<tr>
<td>Antimicrobial properties</td>
<td>Disinfection and biofouling/biocorrosion control without harmful byproducts</td>
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<tr>
<td>Multi-functionality (antibiotic, catalytic)</td>
<td>Fouling-resistant (self-cleaning &amp; self-repairing) membranes that operate with less energy; trap &amp; zap sorbents</td>
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<td>High conductivity</td>
<td>Novel electrodes for selective electro-sorption and energy-efficient electrocatalytic treatment</td>
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When Does Nano Make Sense?

- Where current technologies do not meet current or upcoming regulations;
- When it enhances cost-effectiveness (e.g., faster, less energy, and less materials);
- When one needs easy-to-deploy modular systems with small footprint (remote locations?)
Opportunities in Remediation

- Degradation of recalcitrant compounds (when biodegradation alone is ineffective)
- Higher selectivity towards target contaminants to efficiently utilize the available treatment capacity
- Multifunctionality to address mixed contamination.
- Lower energy requirements for thermal treatment
- Improve source zone remediation (AOPs, ARPs)
- Improve monitoring of remediation progress.
Example 1. Nano-Scale Zerovalent Iron (NZVI)

First used in 2000
70 full scale or pilot tests by 2013
Synergistic Biogeochemical Interactions

$\text{H}_2$ produced by iron corrosion stimulates RDX mineralization: $\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{+2} + \text{H}_2 + 2\text{OH}^-$
RDX Mineralization ($^{14}$CO$_2$) is mediated by bacteria, and Fe$^0$ has a stimulatory effect

Polymer Coatings Mitigate NZVI Aggregation and Toxicity to Bacteria

Dose response of *E. coli* exposed to nZVI

Coating the NZVI Enables Expression of Dehalogenase Genes as it Mitigates Toxicity (Enables Microbial Reductive Dechlorination)

Uncoated nZVI: downregulated

Poly-peptide Coated nZVI: upregulated

Sulfidation overcomes preferential reaction of nZVI with Water

Gu. Wang and Tratnyek, ES&T, 2017; DOI:10.1021/acs.est.7b03604
Example 2: Photocatalysis with nTiO$_2$

Illumination (UV or Sunlight) 

Excitation

Energy transfer/ROS formation

$\text{hv}$

$\text{O}_2$

$\text{O}_2^-$

$\cdot\text{OH}$

$\text{H}_2\text{O}$
Photocatalytic Hydroxylation of Weathered Oil to Enhance Bioavailability and Bioremediation
Photocatalysis Increased Solubilization and Biodegradation of Weathered Oil

* statistically significant \( (p < 0.05) \) after 1-day exposure

Looking Forward: ENMs with multifunctionality could target complex contaminant mixtures
ENMs with high selectivity for contaminants could improve performance and reactive lifetime.
Nano-tracers to delineate distribution of contaminants in the subsurface
ENMs to enhance thermal treatment and decrease energy requirements?
In situ generation of NMs to provide NMs in low-conductivity regions to sequester or degrade contaminants?
Stimuli-responsive ENM that release reactants/biostimulants only when needed
ENMs to enhance rates and performance of bioremediation
CONCLUSIONS

- Some ENMs offer high-performance remediation opportunities as hypercatalysts, oxidants, reductants, and improved separation processes.
- Mainly for above-ground treatment (higher selectivity, lower EEO) but also as pretreatment or biostimulants for enhanced *in situ* bioremediation.
- Need pilot studies to delineate practical applicability and limitations.
Backup Slides
Groundwater circulating wells to emplace ENMs over larger areas?
Feasibility of ENMs to improve specific remediation niches

Subsurface Remedial Activity

Likely
- Liner following Excavation
- In-well Treatment with Highly-Selective Material
- Site Characterization + Source Zone Delineation
- Site Monitoring Following Remedial Action or Monitored Natural Attenuation
- Thermal Treatment
- Permeable Reactive Barriers with Highly-Selective Material
- Adsorptive or Reactive Treatment of Emerging Contaminants (e.g., PFAS)
- Timed-Release Chemical Oxidation Treatment

Unlikely
- Sediment Remediation
- Composting
- Air Sparging
- Low Permeability Media Treatment
- Bedrock Treatment

Efficacy for Contaminant Degradation, Sequestration, and/or Detection
In Situ Chemical Oxidation Using NZVI (Fenton’s Reaction)

Fe$^0$ + O$_2$ + 2H$^+$ → Fe$^{2+}$ + H$_2$O$_2$

Fe$^0$ + H$_2$O$_2$ → Fe$^{2+}$ + 2 OH$^-$

Fe(II) + H$_2$O$_2$ → Fe$^{3+}$ + OH• + OH$^-$
NZVI (1g/L) Preferentially Biostimulated Methanogens, also Dechlorinators after Inhibitory Period

Enhancing Land Farming?

- Contaminated soil is spread as a thin layer (< 0.3 m) on a prepared surface.
- Indigenous microorganisms (bacteria and fungi) remove hydrocarbons.
- Bioremediation is stimulated by aeration and addition of nutrients and moisture.
- Can be slow (6-month cycles).

*TiO₂ pre-treatment could increase number of cycles per year per pit.*
Other Potential Applications (TRL 1-4)

- Nanoparticles that enhance in situ (microwave) heating to enable thermal desorption/smoldering
- Nano-sorbents that selectively bind priority pollutants (higher capacity, faster kinetics)
- Nano-catalysts for faster (pump and treat) advanced oxidation or reductive dehalogenation
- Porous nanocarriers with antimicrobial agents that minimize membrane biofouling
Oxidized GW Pollutants Degraded by NZVI

- **Organics:**
  - Chlorinated solvents (PCE, TCE)
  - Munitions Wastes (TNT, HMX, RDX)
  - PFCs

- **Inorganics:**
  - Nitrate
  - U(VI)
  - Cr(VI)

- **The Dirty Dozen:**
  - Dioxins
  - Furans
  - PCBs
  - HCB
  - DDT
  - Chlordane
  - Toxaphene
  - Dieldrin
  - Aldrin
  - Endrin
  - Heptachlor
  - Mirex