ENVIRONMENTAL REMEDIATION AND SUSTAINABILITY

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Hybrid inorganic-organic nanoparticles to address environmental pollutants

Natural product-based building blocks for sustainability
Oil Spill Response: Current methods of remediation

- Containment
  - Limits exposure
  - Facilitates recovery
- Bulk recovery
  - Current mechanical techniques
- Low concentrations
  - Sheen 0.04 to 50 µm on the water
- Current methods for sheen recovery

Images provided by Jonathan E. Sanders, MECX L.P.
Mode of Recyclable Deployment of MSCKs
Magnetic Shell Crosslinked Knedel-like (MSCK) Nanoparticles Designed for Pollutant Recovery

- Amphiphilic core-shell morphology:
  - Hydrophilic shell allows for suspension in water
  - Hydrophobic core sequesters hydrophobic pollutants

- Shell cross-linked protects micelles and stabilizes vessel
- Entrapped magnetic iron oxide nanoparticles
- High density NP loading

Crosslinking of Magneto Micelles

Well defined core-shell morphology observed in 3D scan

$D_n$: 79 ± 2 nm
$D_v$: 110 ± 50 nm
$D_I$: 200 ± 120 nm

$D_n$: 70 ± 12 nm

2,2’-(Ethylenedioxy)bis(ethylamine), EDCI

$\text{H}_2\text{N}-\text{O}-\text{O}-\text{NH}_2$

$\text{PAA}_{20}-b-\text{PS}_{280}$
Water and remaining oil in tests were decanted into vial to allow for extraction without the presence of MSCKs.

- Extraction of oil with chloroform
- GPC used for quantitative analysis
Sequestration Data and Oil Evaluation

10X oil uptake

- GC/MS analysis of extracted oil

Uptake of all oil fractions

<table>
<thead>
<tr>
<th>Initial MSCK: Oil</th>
<th>Recovery ratio</th>
<th>% oil recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2.8</td>
<td>1:2.1</td>
<td>74.0%</td>
</tr>
<tr>
<td>1:5.1</td>
<td>1:4.4</td>
<td>85.9%</td>
</tr>
<tr>
<td>1:11.5</td>
<td>1:9.6</td>
<td>81.2%</td>
</tr>
<tr>
<td>1:16.8</td>
<td>1:10.2</td>
<td>60.6%</td>
</tr>
</tbody>
</table>

Magnet
Design of Fluorinated MSCK (MSCK-F$_9$) Nanoparticles

**Hydrophilic shell** allows for particle suspension in water

**Fluorinated hydrophobic core** facilitates nanoparticle assembly and provides an environment for capture of fluorinated and/or hydrophobic guests

PFOA is an environmentally-and biologically-persistent pollutant

**Iron oxide nanoparticles** entrapped in the core provide magnetic responsiveness

**Shell crosslinks** protect the morphological assembly while allowing for expansion and contraction

Hypothesis: Greater removal of PFOA due to size difference of nanoparticles ca. 60, 72, 40, and 42 nm in diameter.

At 35% PFOA recovery, ca. 0.35 mg PFOA/mg MSCK-F_9, PFOA removal is two orders of magnitude better than other reported nanomaterials!
New Multi-compartment MSCK Nanoclusters

- Satellite amphiphilic shell crosslinked knedel-like (SCK) nanoparticles
- SCK hydrophilic shell allows for water solubility and covalent linkage to inorganic component
- Hydrophobic core preferentially sequesters hydrophobic pollutants
- Incorporating SCKs with differing compositions offers enhanced tunability of material for targeted remediation
- Large inorganic core for magnetic response of the material

Magnetic Hybrid Networks (MHNs)

[Yingchao Chen w/Darrin Pochan]
Performance of the MHNs is Compromised in the Presence of Brine

- Formation of an emulsion was observed upon hand-shaking of the water/dodecane/MHN mixture.

**Loading Capacity Ratio of the MHNs Towards Dodecane**

- Emulsification ability can be compromised in saline environments.
- Maximum Capacity in water = *ca.* 30 mg of dodecane per 1 mg of MHNs
- Maximum Capacity in brine = *ca.* 17 mg of dodecane per 1 mg of MHNs
The MHNs Assemble at the Droplet Interface to Stabilize the Emulsion

- FITC was covalently bound to the MHNs
- Emulsions were formed by hand-shaking the dodecane/water/MHN mixture
• Nile red was dissolved in dodecane
• MHNs were not labeled with FITC
• Sample was excited with at a wavelength of 543 nm, the MHNs exhibit red fluorescence
The Emulsion Droplets are Magnetically-active

Potential Concerns with Unrecovered Nanoparticles

Decanting of remaining pollutant
c. 1 h

Recovery of Deployed Materials via Magnetic Action

- ca. 93% recovery after deployment
- ca. 90% recovery after organic wash
Idealized Polymer Life Cycle

Monomers (renewable resources)

Polymerization

Polymers (functional performance)

Degradation

Degradation products (biological/environmental resorption and clearance)

Benign (if lost in the environment, intact)
Current Status for Wooley Group Natural Product-based Polymers

Linear Polycarbonates w/control Over Regiochemistry

Glucose & other sugars

SUGAR PLASTICS™

Quinic Acid

Linear Polycarbonates and Block Copolymers by ROPs

Crosslinked Networks

Honokiol

Ferulic Acid

Amino Acids

Quercetin
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