Transport of Nanoparticles in Porous Media

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Nanoparticles

- Unique electronic, optical, thermal and photoactive properties
- Currently found in ~80 consumer products and over 600 raw materials
- Applications in coatings, computers, clothing, cosmetics, sports equipment and medical devices
Semiconductor Manufacturing

- Nanoparticles utilized in:
  - CMP
  - Immersion Lithography
  - CVD

- Common Oxide NPs:
  - Silica
  - Alumina
  - Ceria
  - Titania
  - Zirconia

Effluent Nanoparticle Concentration
50 – 500 mg/L
Previous Work

**Primary Treatment**
- Sewage Inlet
- Bar Screen
- Grit Chamber
- Primary Clarifier
- Sludge Digestion

**Secondary Treatment**
- Bioreactor
- Secondary Clarifier
- Return Sludge

**Tertiary Treatment**
- Filter & UV Disinfection
- Effluent

**Sludge Disposal**
Previous Work

### Removal Efficiency

<table>
<thead>
<tr>
<th></th>
<th>Settling</th>
<th>Biosolid</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>---</td>
<td>50.7%</td>
<td>50.7%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>29.3%</td>
<td>29.6%</td>
<td>58.9%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>---</td>
<td>17.2%</td>
<td>17.2%</td>
</tr>
</tbody>
</table>
Previous Work

Sewage Inlet → Bar Screen → Grit Chamber → Primary Clarifier → Sludge Digestion → Return Sludge → Secondary Clarifier → Bioreactor

Effluent → Filter & UV Disinfection → Tertiary Treatment
Porous Media Filtration

• One of the oldest water treatment technologies dating to ~2000 B.C.

• Applications in drinking water and wastewater treatment
  – Removal of particulate matter
  – Often used with coagulants

• Also may be used to model transport in the water table
Porous Media Filtration

Removal Mechanisms

Aggregation and Diffusion/Adsorption are expected to dominate
Aggregation Principles

- DLVO Theory Interactions
  - van der Waals
  - Electrical double layer
- Steric Interactions
- Hydration
Nanoparticle Specific Principles

• Heterogenous Collector Surfaces
• Primary Energy Minimum
• Shape Effects
## Aggregation Studies

<table>
<thead>
<tr>
<th>Particle</th>
<th>Size</th>
<th>Concentration</th>
<th>Parameters Studied</th>
<th>Conclusions</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>4-6 nm</td>
<td>80 mg/L</td>
<td>4.5 – 16.5mM NaCl 12.8mM CaCl₂ pH 4.8 – 8.2</td>
<td>Divalent cations increase aggregation rate</td>
<td>[1]</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>20 nm</td>
<td>10 – 200 mg/L</td>
<td>10-100 mg/L SRHA</td>
<td>HA adsorption contributes to stability</td>
<td>[2]</td>
</tr>
<tr>
<td>SiO₂/Fe₃O₄</td>
<td>56 nm</td>
<td>2470 mg/L</td>
<td>2-3 µmol/m² Tween 20</td>
<td>Non-ionic Surfactant results in decreased stability</td>
<td>[3]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>5 nm</td>
<td>1 mg/L</td>
<td>5 – 100mM NaNO₃ 0.2 – 5 mg/L FA pH 2 – 8</td>
<td>Aggregation near pH of PZC; FA increased stability</td>
<td>[4]</td>
</tr>
</tbody>
</table>
Adsorption Principles

• Transport governed by Brownian diffusion

• Deposition dependant on:
  – Particle Size
  – Collector Size
  – Solution Chemistry
  – Zeta Potential
  – Hamaker Constant

• Attachment Efficiency

\[ \eta = \alpha \eta_0 \]
# Adsorption Studies

<table>
<thead>
<tr>
<th>Particle</th>
<th>Size</th>
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<th>Collector</th>
<th>Parameters</th>
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</tr>
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<tbody>
<tr>
<td>CuO</td>
<td>372nm (&lt;50 prim.)</td>
<td>9 mg/L</td>
<td>2-D Etched Glass</td>
<td>0.01M NaCl pH 7 0.01 – 0.1% SDS</td>
<td>SDS enhances elution</td>
<td>[5]</td>
</tr>
<tr>
<td>SiO₂</td>
<td>57 nm 135 nm</td>
<td>10 mg/L</td>
<td>Glass Beads (355μm)</td>
<td>0.01M NaCl pH 7</td>
<td>Low affinity; Larger particles better retained; no impact due to flow rate change</td>
<td>[6]  [7]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>&lt;0.1μm</td>
<td>50-100 mg/L</td>
<td>Quartz Sand (200μm)</td>
<td>0.01M NaCl pH 4.5</td>
<td>High particle retention</td>
<td>[8]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>32 nm</td>
<td>50 mg/L</td>
<td>Quartz Sand (650μm)</td>
<td>I = 10⁻³ – 10⁻¹ M pH 3, 6, 8</td>
<td>Retention increased with increasing ionic strength</td>
<td>[9]</td>
</tr>
<tr>
<td>TiO₂ ZnO CuO</td>
<td>&lt;100 nm &lt;100 nm &lt;50 nm</td>
<td>n/a</td>
<td>Glass Beads</td>
<td>0.01-0.1M NaCl pH 7, 12 60mg/L HA</td>
<td>Mobility increases with addition of HA</td>
<td>[10]</td>
</tr>
</tbody>
</table>
Needs in Current Transport Study

• Highly uniform particle size distribution
  – Ability to compare size effect between nanoparticles

• Real-time aggregation and deposition measurement

• Cohesive model for nanoparticle removal
  – Accounting for aggregation in adsorption
  – Including effect of common contaminants
• Fluorescent Core/Shell Silica Nanoparticles

- **Dye Precursor**
  - APTES and NHS-Fluorescein in Ethanol

- **Core**
  - TEOS in ammonia and ethanol solution

- **Shell**
  - TEOS aliquots added sequentially to desired size

**Final Diameter controllable**
Nanoparticle Synthesis

- Fluorescent Core/Shell Silica Nanoparticles

Size Distribution

23.4 ± 8.5 nm

Percentage

Diameter (nm)

100 nm
New Experimental Setup

• Measurement of Light Absorption or Fluorescence
• On-line measurement of concentration and particle size
Uptake Model

• Assuming spherical primary particles:

\[
\frac{\partial \Gamma}{\partial \tau} = \frac{1}{Pe} \frac{\partial^2 \Gamma}{\partial x^2} - \frac{\partial \Gamma}{\partial x} - \alpha [K_a \Gamma(1 - \theta) - K_d \theta]
\]

\[
\frac{\partial \theta}{\partial \tau} = K_a \Gamma(1 - \theta) - K_d \theta
\]

**Variables**

- \(\Gamma\) = relative nanoparticle concentration
- \(\theta\) = fractional surface coverage
- \(x\) = dimensionless reactor length
- \(\tau\) = dimensionless time

**Fit Parameters**

- \(K_a\) = 1\(^{st}\) order adsorption MXC
- \(K_d\) = 1\(^{st}\) order desorption MXC
References


