Fate of CMP Nanoparticles During Wastewater Treatment

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Nanoparticles (NPs): Materials with at least one dimension of 1 to 100 nm

Adapted from Andrew Schneider’s “Amid nanotech’s dazzling promise, health risks grow”, 2010
What makes nanomaterials interesting?

- **Small size:**
  Surface area, atoms exposed

- **Shape (spheres, flakes, tubes, rods, etc.):**
  Pattern of molecular bonds

- **Chemical composition:**
  Crystal structure, pollutants on surface

- **Solubility:**
  Dispersion or agglomeration

**Quantum effects and bulk properties!!**
Benefits associated to nanomaterials

- **Environmental:**
  Pollution prevention, remediation/treatment

- **Water:**
  Improve water quality

- **Energy:**
  Increase efficiency, production, and storage

- **Materials:**
  Increase selectivity in chemical reactions, replacement of toxic materials

- **Agriculture:**
  Genetic improvement of plants and animals
Introduction: Nanoparticles market

Household products containing nanomaterials:

- Sporting goods
- Food packing materials
- Stain-resistant clothing
- Healthcare products
- Cosmetics

Major nanomaterials consumers:

- Semiconductor industry:
  - Chemical-mechanical planarization (CMP)
  - Photolithography
- Automotive catalysts
- Magnetic recording media
- Sunscreens

Developed by the U.S. Air Force

1 trillion dollar market by 2015
NSF, 2001
Little is known about the fate of nanoparticles in the environment and possible toxic effects on living organisms.
### Introduction: Potential risks

**Exposure:**
- Inhalation
- Ingestion
- Dermal

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fullerenes ($C_{60}$)</td>
<td>Antibacterial; oxidative stress; may induce DNA damage in plasmids</td>
</tr>
<tr>
<td>Titanium dioxide (TiO$_2$)</td>
<td>Antibacterial; oxidative stress; may damage DNA; tissue thickening</td>
</tr>
<tr>
<td>Zinc oxide (ZnO)</td>
<td>Oxidative stress; may damage DNA; pulmonary adverse effects</td>
</tr>
<tr>
<td>Cerium oxide (CeO$_2$)</td>
<td>Oxidative stress; thickening of heart tissue, could bind to cell membrane of Gram-negative bacteria</td>
</tr>
</tbody>
</table>
Introduction: Fate of NPs in the Environment

- It is largely unknown.
- Agglomeration/sedimentation and partitioning onto solids are thought to control their fate in the environment.
- Could travel long distances if mixed with stabilizers or attached to organic matter.
How do nanomaterials get to wastewater treatment plants (WWTP)?

Muller and Nowack, 2008, estimated TiO$_2$ and Nano-Ag reaching WWTP
39% nano-Ag
64% TiO$_2$

Adapted from http://www.epa.gov
Introduction: Wastewater treatment

WWTPs remove **harmful organisms** and **pollutants**

**Primary treatment**
Remove large solids (rags and debris) and smaller inorganic grit

**Secondary treatment**
Removes organic contaminants using microorganisms to consume biodegradable organics

**Tertiary treatment**
Removes nutrients and may include disinfection of the effluent

Introduction: Wastewater treatment

PRIMARY TREATMENT

Screening/Grit removal → Primary Settler

SECONDARY TREATMENT

Biological Treatment → Secondary Settler → Disinfection → Effluent

Sludge → Anaerobic digestion → Disposal
Introduction: Wastewater treatment

Returned activated sludge (RAS)
High water content
Forms flocs
Possible removal mechanisms

**Gravity Settling**

**Entrapment by A/S flocs**

**Ad- and/or absorption**

**Intake**
No conclusive results have yet been obtained

- Activated sludge process attained high removal of CeO$_2$ from **synthetic medium** (Limbach et al. 2008)

- Iron oxide (Fe$_3$O$_4$) cored SiO$_2$ NPs **coated with a nonionic surfactant** effectively **removed during primary treatment**. **Unfunctionalized** NPs **escaped** with the effluent (Jarvie et al, 2009).
Objectives

- To investigate the removal of CeO$_2$ nanoparticles (NPs) in municipal wastewater during activated sludge treatment

- To elucidate the mechanisms responsible for their removal from aqueous dispersions
Lab-scale secondary treatment

Aeration tank:
\[ V_{\text{reactor}} = 1.19 \text{ L} \]
\[ \text{HRT} = 9 \text{ to } 10 \text{ hrs} \]

Settler:
\[ V_{\text{reactor}} = 0.6 \text{ L} \]
\[ \text{HRT} = 5 \text{ to } 6 \text{ hrs} \]

The system was operated under two different conditions:

- **Synthetic wastewater**
  Composition according to OECD

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peptone</td>
<td>220</td>
</tr>
<tr>
<td>Meat extract</td>
<td>150</td>
</tr>
<tr>
<td>Urea</td>
<td>10</td>
</tr>
<tr>
<td>$\text{K}_2\text{HPO}_4$</td>
<td>8</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>200</td>
</tr>
</tbody>
</table>

- **Real wastewater**
  Primary-treated wastewater collected in a weekly basis from a local WWTP
NP Stock:

CeO$_2$ (50nm)

Concentrated stock prepared by sonication (pH = 3.4)

Concentrated stock diluted in acidic water (pH = 3.4)

Transmission electron microscope image of nano-size ceria with average particle size 50 nm
Fate of nanoparticles

Inductively coupled plasma-optical emission spectroscopy instrument (ICP-OES)

- **Total Ce concentration**
  - Microwave-assisted digestion
  - Reduces interference by organic matter

- **Filtered Ce concentration (< 200 nm)**
  - Directly measured in ICP-OES

- **Scanning electron microscopy (SEM)**
  - Image the sample by scanning it with a high-energy electron beam

ICP-OES

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Reactor performance

- **Chemical oxygen demand (COD)**
  - Indirect measurement of the organic content
  - Sample + Strong oxidant $\xrightarrow{150^\circ C}$ Spectrophotometer

- **Acetic acid removal**
  - Measured by Gas-Chromatography with Flame Ionization Detector (GC-FID)
  - Agilent 7890A GC
Results: Average particle size ($\text{CeO}_2$)

Diameter Size Average (nm)

$[\text{CeO}_2] = 200$ ppm

pH = 3.46

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Results: Stability particle size (CeO$_2$) in aqueous suspension

CeO$_2$ NP aggregate in municipal wastewater

Average Particle Size (nm)

- CeO$_2$ (pH 3.2)
- CeO$_2$ (pH 7.5)
- CeO$_2$ + Real WW (pH 7.5)
- CeO$_2$ + Synthetic WW (pH 8.02)
### Results: Average particle size (CeO$_2$)

#### Average particle size distribution in different media

<table>
<thead>
<tr>
<th>Sample</th>
<th>Avg Particle size (nm)</th>
<th>Std Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$ (pH 3.2)</td>
<td>132</td>
<td>1</td>
</tr>
<tr>
<td>CeO$_2$ (pH 7.5)</td>
<td>9035</td>
<td>46</td>
</tr>
<tr>
<td>CeO$_2$ + Real WW (pH 7.5)</td>
<td>5567</td>
<td>114</td>
</tr>
<tr>
<td>CeO$_2$ + Synthetic WW (pH 8.02)</td>
<td>175</td>
<td>6</td>
</tr>
</tbody>
</table>

#### Average particle size distribution of nano-sized CeO$_2$ in acidic media (pH 3.2)

- Average particle size (nm): $132 \pm 1$
- Zeta potential (mV): $44.5 \pm 1.1$
Results: Fate of CeO$_2$

Total Ce Removal by Activated Sludge Treatment

- 95.7% average removal

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Results: Fate of CeO$_2$

< 200 nm CeO$_2$ Removal by Activated Sludge Treatment

98.7% avg removal

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Results: Fate of CeO$_2$

< 25 nm CeO$_2$ Removal by Activated Sludge Treatment

- 97.2% avg removal
**Results: Fate of CeO$_2$**

**Total Ce removal (Real WW)**

- 95.7% avg removal

**Ce < 200 nm removal (Real WW)**

- 98.7% avg removal

**Total Ce removal (Synthetic WW)**

- 94.3% avg removal

**Ce < 200 nm removal (Synthetic WW)**

- 78.9% avg removal

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Results: Reactor performance

Removal of Organic Matter by Activated Sludge Treatment (Real Wastewater)

Fresh wastewater batch

COD concentration (mg/L)

Time (days)

Total COD in

Total COD out

66.8% avg removal

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Acetate Removal by Activated Sludge Treatment (Real Wastewater)

Results: Fate of CeO$_2$

93.4% avg removal
Results: Reactor performance

Volatile Suspended Solids in the Aeration Tank

Day 0
Day 49
Day 58

Concentration (gVSS/L)
Results: CeO$_2$ + sludge

Original sludge (t= 0 day)

Bioreactor
Results: CeO$_2$ + sludge

Sample from Bioreactor

Protozoa

Extracellular material

Element microanalysis by energy dispersive X-ray spectroscopy (EDS)
Conclusions

- CeO$_2$ is highly removed during secondary treatment. Only a small fraction of the NPs (< 5%) detected in the effluent.

- Neutral pH values promote agglomeration of NPs dramatically increasing their average particle size compared to the size in a pH 3 solution.

- CeO$_2$ did not cause microbial inhibition, as demonstrated by the continuous removal COD and acetate.
Fate of aluminum oxide (Al₂O₃) NPs in municipal wastewater during activated sludge treatment.
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