Fate of Silica Nanoparticles during Secondary Wastewater Treatment

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NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
Engineered nanoparticles

- Nanoparticles (NPs) are particles sized in less than 100 nm.

**Unique Properties of NPs**

- Small size
- High specific surface area
- Optical properties
- Semiconductor properties.....
Applications of SiO$_2$ nanoparticles

- CMP slurries
- Printer toners
- Biosensors

- Personal care products
- Varnishes
- Food additive

- Diagnostic and biomedical research

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EHS Concerns about SiO$_2$ NPs

- Multiple studies indicate that some SiO$_2$ NPs cause toxicity.
- Recent studies suggest that fumed SiO$_2$ is more toxicity than colloidal SiO$_2$ (Zhang et al. 2012).


Impact of fumed SiO$_2$ (A) and colloidal SiO$_2$ (B) on viability of human bronchial epithelial cells
CMP NPs & Wastewater Treatment

Fab

On-site treatment

Sewer system

Municipal wastewater treatment plant
Activated Sludge (A/S) Process

Biodegradable Organic Matter + O₂ → Cells + H₂O + CO₂

(biomass)

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Biological wastewater treatment: Possible NP removal mechanisms

**Gravity Settling**

**Entrapment by A/S flocs**

**Adsorption**

**Intake (?)**
Fate of SiO$_2$ NP during municipal wastewater treatment

- Lack of reports on the fate of SiO$_2$ NP during biological wastewater treatment

- Iron oxide (core)-SiO$_2$ (shell) NPs not removed by primary treatment (settling process, prior to biological treatment). NPs coated with nonionic surfactant effectively removed (Jarvie et al, 2009).
  
  - NP conc. used very high!! 2470 mg/L

High background SiO$_2$ levels in wastewater can interfere with analysis of SiO$_2$ NPs

- Natural waters contain dissolved and suspended forms of silica
- Dissolved silica in natural waters varies from ca. 1–3 mg/L in mountain lakes to 50–300 mg/L in well waters in volcanic and oil production fields (Ning 2002)*
- Fluorescent SiO$_2$ NPs valuable to study the fate of nano-SiO$_2$ during wastewater treatment.

Objectives

• To investigate the fate of SiO$_2$ NPs during conventional biological wastewater treatment.

• To study the mechanisms contributing to the removal of SiO$_2$ NPs in the activated sludge process.
SiO$_2$ NP Synthesis: Water-in-Oil Microemulsion Method

Fluorescent core, SiO$_2$ shell NP

Adapted from Bonachi et al. 2011. Angew. Chem. Int. Ed. 50, 4056 – 4066

Fluorescent core, SiO$_2$ shell NP

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(tetraethoxysilane, TEOS)
Synthesis of Fluorescent SiO$_2$ Nanoparticles

**Fluorescence Spectra for Rhodamine B ITC**

![Fluorescence Spectra for Rhodamine B ITC](image)

- **Excitation**
  - Max. 584 nm
- **Emission**
  - Max. 579 nm

**Rhodamine B isothiocyanate**

Sentra et al. 2001. Anal. Chem. 73(20):4988-4993,
Fluorescent SiO$_2$ NPs: TEM

Average particle size: 88 ± 7 nm

Polydispersity: 0.315
Fluorescent SiO$_2$ NPs: Zeta potential vs pH
Fluorescent SiO$_2$ NPs: Zeta potential vs pH
Fluorescent SiO$_2$ NPs: Average Particle Size vs. pH
Lab-Scale Activated Sludge Bioreactor

Aeration tank:
\[ V_{\text{reactor}} = 1.19 \text{ L} \]
HRT \[ = 9.9 \text{ hrs} \]

Settler:
\[ V_{\text{reactor}} = 0.6 \text{ L} \]

Temp: 22°C

## Synthetic Wastewater

### Composition according to OECD guidelines*

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peptone</td>
<td>160 mg/L</td>
</tr>
<tr>
<td>Meat extract</td>
<td>110 mg/L</td>
</tr>
<tr>
<td>Urea</td>
<td>30 mg/L</td>
</tr>
<tr>
<td>K$_2$HPO$_4$</td>
<td>28 mg/L</td>
</tr>
<tr>
<td>NaCl</td>
<td>7 mg/L</td>
</tr>
<tr>
<td>CaCl$_2$.2H$_2$O</td>
<td>4 mg/L</td>
</tr>
<tr>
<td>Mg2SO$_4$.7H$_2$O</td>
<td>2 mg/L</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>150 mg/L</td>
</tr>
<tr>
<td>COD concn.</td>
<td>270 mg/L</td>
</tr>
</tbody>
</table>

**F-SiO$_2$**  
7.9 ± 1.7 mg/L

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* OECD GUIDELINE FOR THE TESTING OF CHEMICALS  
Simulation Test - Aerobic Sewage Treatment:  
303 A: Activated Sludge Units. OECD 303, January 2001
Reactor Monitoring

**Organic matter**
Chemical Oxygen Demand, colorimetric micro-method

**Biological solids (Biomass)**
Determination of volatile suspended solids (VSS)

**SiO$_2$**
- Fluorescence measurement

**pH**

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Particle size and zeta potential of SiO$_2$ NPs in wastewater

Average size: 168-178 nm

PSD & Zeta Potential (DLS)
Fluorescent SiO$_2$ NPs: Leaching behavior in wastewater
Operation and Performance of the Activated Sludge Process

pH- influent = 7.4 ± 0.2  
COD removal= 93 ± 5%

pH effluent = 7.1 ± 0.4
Removal of SiO₂ NPs by Activated Sludge Treatment

![Graph showing SiO₂ removal over time with NPs addition](image)

- SiO₂ Conc. (mg L⁻¹) vs. Time (d)
- SiO₂ removal (%) vs. Time (d)

34.5% removal of SiO₂ NPs
Suspension of fluorescent SiO$_2$ NPs stable in the synthetic OECD wastewater
Association of SiO$_2$ with Activated Sludge

Bright-field (A) and epifluorescence (B) images of activated sludge biomass.
Conclusions

- Continuous-flow bioreactor studies demonstrated that biological treatment (i.e. activated sludge) has a limited ability to remove SiO$_2$ NPs from the synthetic wastewater used.

- Removal of SiO$_2$ NPs was mainly due to NP association with the biomass. The suspension of fluorescent SiO$_2$ NPs was stable in the synthetic wastewater used in this study.

- SiO$_2$ did not cause microbial inhibition, as demonstrated by the high COD removal efficiency.
Future plans

- Investigate the fate of CMP NPs and III/V species (In, Ga, As) in CMP effluents during wastewater treatment.
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Related Publications


Thank you!