Monitoring Fate and Behaviour of Nanoceria under relevant Environmental Conditions

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Introduction

Wagner et al. Angew. Chem. Int. Ed. 2014,
### Table 1: Global production volumes of ENMs

<table>
<thead>
<tr>
<th>ENMs Type</th>
<th>ENM production (tons per year)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>World wide</td>
</tr>
<tr>
<td>TiO₂</td>
<td>&gt;60,000</td>
</tr>
<tr>
<td>ZnO</td>
<td>&gt;1,400,000</td>
</tr>
<tr>
<td>CeO₂</td>
<td>0.55-2800</td>
</tr>
<tr>
<td>SiO₂</td>
<td>55-55,000</td>
</tr>
<tr>
<td>Fullerence</td>
<td>0.15-80</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>&gt;4065</td>
</tr>
<tr>
<td>Quantum dots</td>
<td>0.6-5.5</td>
</tr>
<tr>
<td>Nano Ag</td>
<td>&gt;550</td>
</tr>
</tbody>
</table>

Global Distribution of ENMs Type Release per Continent to air, water, soil, and landfills

Keller and Lazareva, EST, 2013
Motivation for the study

• Why the need:
  • There’s a dramatic increase in production of ENMs
  • Concerns over their release in the environment
  • Establish pathways for ENMs fate, and transport in aquatic systems

• Impact and relevance
  • Enhance collective understanding of ENMs fate, behaviour, and effects in environmental systems to support safe, responsible and sustainable exploitation of nanotechnology-driven capabilities
Nanoceria Applications

The increasing applications will inevitably lead to CeO2 release into the environment, which will impose risks on humans and ecosystems. Listed one of the 14 key ENMs of focus by OECD.
Other applications of nanoceria are:

- Biomedical applications such as its use as an antioxidant (Chen et al. 2013)
- UV-Shielding (Dao et al. 2011), e.g. application as a sunscreen component (Zholobak et al. 2011)
- *Used in toner formulation* (Bello et al. 2013)
- Used in catalysts in petroleum refining, in the fluid catalytic cracking process (FCC) (Global Market for Nanomaterials, 2012)

Toxicity studies of CeO₂ in environmental systems

ordinary heterotrophic organisms (OHO) and ammonium oxidising bacteria (OAB)

García et al. J. Hazard. Mat., 2012
Likely scenarios of ENMs fate and transformation in environment

Lowry et al., EST, 2012
Objectives

• To investigate the effect of abiotic factors: pH and natural organic matter (NOMs)

• To investigate the stability in freshwater system with respect to aggregation/agglomeration

Data from studies chiefly aided to elucidate fate and behavioural of nanoceria in aquatic systems
Experimental Design

CeO\textsubscript{2} ENPs

Hydrodynamic characterization of CeO\textsubscript{2} size, and zeta potential

Physicochemical properties as influenced by pH, concentration and agglomeration/aggereation effects

Exposed ENPs in artificial water using alginate and humic acid as NOMs

Exposure in freshwater samples after 0.2 and 0.45 um membrane
### Freshwater characterization data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (stdev.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.05-7.54 (0.15)</td>
</tr>
<tr>
<td>DOC mg/L</td>
<td>3.2-3.77 (0.17)</td>
</tr>
<tr>
<td>Na$^+$ mg/L</td>
<td>13 (0.03)</td>
</tr>
<tr>
<td>Ca$^{2+}$ mg/L</td>
<td>10.67 (0.47)</td>
</tr>
<tr>
<td>Mg$^{2+}$ mg/L</td>
<td>7.93 (0.05)</td>
</tr>
<tr>
<td>SO$_4^{2-}$ mg/L</td>
<td>7.97 (0.17)</td>
</tr>
<tr>
<td>Cl$^-$ mg/L</td>
<td>0.02 (0.005)</td>
</tr>
</tbody>
</table>
Characterization of CeO$_2$ NPs

<table>
<thead>
<tr>
<th>Method</th>
<th>Size (nm)</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTA</td>
<td>117 ($\pm$3.6)</td>
<td>11.98 ($\pm$1.5)</td>
</tr>
<tr>
<td>Zetasizer</td>
<td>136.7 ($\pm$5.5)</td>
<td>10.4 ($\pm$0.36)</td>
</tr>
</tbody>
</table>
Effect of pH

![Chart showing the effect of pH on hydrodynamic size (nm) and zeta potential (mV). The x-axis represents pH, while the y-axes represent hydrodynamic size and zeta potential. The chart indicates a decrease in hydrodynamic size and an increase in zeta potential as pH increases from 0 to 12.](image-url)
Effect of NOM types on size of CeO$_2$NPs

![Graph showing the effect of NOM types on the size of CeO$_2$NPs.](image)

- **ALG (5mg/L)**
- **ALG (15mg/L)**
- **ALG (25mg/L)**
- **HA (5mg/L)**
- **HA (15mg/L)**
- **HA (25mg/L)**

**x-axis:** Concentration (mg/L)
**y-axis:** Particle size (nm)

Legend:
- **ALG**
- **HA**
- **T0**
- **T1**
- **T2**
Effect of NOM on Zeta Potential

- Chart showing the effect of NOM on zeta potential with concentrations in mg/L for ALG, ALG (15 mg/L), HA, HA (15 mg/L), and HA (25 mg/L).
- Graph showing the decrease in zeta potential with concentration for ALG and HA.

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NTA results

- Zeta potential (mV)
- Particle size (nm)

Concentration (mg/L)

T0 (HA) • T1 (HA) • T0 (ALG) • T1 (ALG) • zeta potential

PSD (nm)
### Behaviour of CeO$_2$NPs along pH$_{PZC}$ range

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Size (nm)</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>5.99</td>
<td>158 ($\pm$11.9)</td>
<td>8.68</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>104 ($\pm$3)</td>
<td>12.05</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>122 ($\pm$4.4)</td>
<td>9.58</td>
</tr>
<tr>
<td>FW (T0)</td>
<td>7.34</td>
<td>99 ($\pm$2.4)</td>
<td>-18.98</td>
</tr>
<tr>
<td>FW (T1)</td>
<td>7.58</td>
<td>108 ($\pm$4)</td>
<td>-27.5</td>
</tr>
</tbody>
</table>

### Graphs

- **Particle size (nm)**
  - DI
  - ALG
  - HA
  - FW

- **Zeta potential (mV)**
  - FW
  - HA
  - ALG
  - DI

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![CSIR Logo](csir_logo.png)

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Summary

• CeO$_2$ NPs are highly unstable and tend to settle out of aqueous phase
• NOM show to stabilise the NPs though significant agglomeration occurs
• In freshwater, aggregation/agglomeration occurs still at nano scale depending on the conditions
Future work

• Monitor aggregation and agglomeration rates at longer duration period and whether deagglomeration/deaggregation is possible for CeO$_2$ NPs
• Study dissolution rates
• Stabilization and surface functioning of the NPs
Acknowledgements