Toxicity of Silver Nanoparticles to Green Algae – Towards a Biotic Ligand Understanding

Laruelle, Sacha; Sørensen, Sara Nørgaard; Cupi, Denisa; Engelbrekt, Christian; Veinot, Jonathan; Baun, Anders

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Introduction

Silver is the most common material in commercial products integrating some form of nanotechnology. It is mostly used for its antimicrobial and antibacterial properties.

Increasingly popular, silver nanoparticles (AgNPs) are more and more likely to be released to the aquatic environment during the manufacturing, use or waste lifecycle stages of nanoproducts.

However, still little is currently known on the toxicity of AgNPs and the mechanisms of their toxicity.

The aim of this study was to evaluate how nanoparticle properties and water medium parameters influence the toxicity of silver nanoparticles and whether changes in toxicity could be explained using conceptual models such as the Biotic Ligand Model.

Results

Concentration–response curves for the silver compounds (excluding AgNP+MUDA) in closed tests at pH 7

Concentration–response curves for the silver compounds (excluding AgNP+MUDA) in closed tests at pH 8

Algal growth inhibition toxicity tests with AgNPs

<table>
<thead>
<tr>
<th>Silver nanoparticles</th>
<th>AgNP+Citrate</th>
<th>AgNP+MUDA</th>
<th>NM-300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer size (nm)</td>
<td>30</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>Z-average measured by DLS (nm)</td>
<td>42.1</td>
<td>38.5</td>
<td>29.3</td>
</tr>
<tr>
<td>Diameter measured by NTA (nm)</td>
<td>65</td>
<td>81</td>
<td>71</td>
</tr>
<tr>
<td>Diameter measured by TEM (nm)</td>
<td>4.5 - 46.5*</td>
<td>33.4</td>
<td>2.6 - 15.4*</td>
</tr>
</tbody>
</table>

2 peaks observed

- Silver nanoparticles with citrate (AgNP+Citrate) and mercaptoundecanoic acid (AgNP+MUDA) cappings and reference OECD silver nanoparticles (NM-300K) were used. Their toxicity was compared with that of silver nitrate.
- Standard (ISO 8692:2004) growth inhibition tests with unicellular freshwater green algae Pseudokirchneriella subcapitata were carried out in open and closed tests at pH 7 and 8.
- K+, Li+ and Ca2+ cation additions were made.

Outlook – A new approach to testing NPs?

The sensitivity of an alternative short-term (2h) algal test, using C-14 incorporation as endpoint was studied.

This 2h test was found to be as sensitive as the standard (ISO) test, when testing the toxicity of Ag+ (AgNO₃). Statistically similar EC₅₀ values were obtained using the two methods (closed test pH 7).

Besides from being fast, easy and efficient - this test method may also circumvent the challenges related to the instability of nanoparticles in solution. Minimizing exposure time is expected to minimize the effects of time-dependent processes such as aggregation, sedimentation, ion release and interactions between NPs and media components/test organisms – suspected contributors to the poor reproducibility in nanotoxicological studies.

Further research will assess the appropriateness of this method.

Conclusions

- Concentration-response curves could be built for AgNP+Citrate and NM-300K, whereas AgNP+MUDA did not exhibit any significant toxicity in the tested concentration ranges.
- AgNPs were consistently less toxic than AgNO₃ based on total silver concentrations.
- All silver compounds (except AgNP+MUDA) showed a decrease in toxicity from pH 8 to 7, in accordance with the Biotic Ligand Model.
- This could not be reproduced with competing cation additions, possibly because of the low concentrations used. Li+ addition may create a combination effect with silver nitrate, actually increasing the toxicity.
- A 2h algal test with AgNO₃ had the same sensitivity as the standard ISO test - and may circumvent some of the challenges related to ecotoxicological testing of nanoparticles.