Nanostructures down the drain: perception and reality

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Abstract
Public concern over the discharge of nanomaterials to wastewater treatment systems has caused at least one product to be taken off the market. This paper discusses wastewater discharges containing nanoscale materials and potential risks [1], considering:

1. Mass balance approach: Preliminary research suggests the levels of wastewater discharges of some nanomaterials [2], the extent to which those materials are treated in publicly owned treatment works (POTW) [3], and the toxicity levels of such materials to certain test organisms. This paper uses a mass balance approach to synthesize the results of such research and estimate the potential discharges to POTW. It also discusses the toxicological implications of these discharges.

2. Regulatory restrictions on discharges. The U.S. Environmental Protection Agency (EPA) is evaluating how best to adapt environmental regulations developed for "conventional" pollutants to nanomaterials [4]. This paper briefly discusses the regulatory and policy approaches being considered.

Introduction
With some 600 commercial products reportedly on the market now [5] and more under development, nanomaterials are entering municipal wastewater treatment plants. That realization has heightened concerns about the effects of these materials on treatment plants and the potential for release of free nanoscale materials into the environment. No comprehensive studies on the problem have yet been published.

Nanomaterials could be included in wastewater discharges as a result of several scenarios:

1. Manufacturing processes involving nanoscale materials could discharge these materials.

2. The use as intended of certain products that contain a nanoscale material component could result in discharges to a POTW or to water bodies.

3. The potential for nanoscale materials embedded in decomposing consumer products discreted in landfills to migrate into the environment is not clear.

4. Uncertainties regarding these discharges, and those surrounding the risks nanoscale materials may pose to human health and the environment could inspire a backlash against specific nano-enabled products, particularly consumer products.

The concentration of a nanomaterial in wastewater depends primarily on:

1. The amount produced or used locally.

2. Whether the nanomaterials are fixed in a matrix or free.

3. The concentration of the free nanomaterial in the commercial product.

4. The fraction that is washed down the drain.

5. The degree of agglomeration or adsorption which occurs in aqueous solution that changes the form of the nanoparticle or removes it from solution.

6. The extent of dilution.

The case study to the right illustrates the issue.

Case study
How much silver could reach a wastewater treatment plant?

Preliminary mass balance on silver generation during laundry cycle using the SilverCare™ function:

1. Generation

Samsung describes SilverCare™ washing machine option in different ways [6-9]:

- 400 billion silver ions generated during each wash cycle; OR

- "Electro-culants nano-shave two silver plates the size of large chewing gum sticks", which reportedly last for 3,000 wash cycles; OR

- Use of washing machine reportedly releases 0.05 grams per year. Are these nano silver particles or ionic silver?

Key and Maas [10] indicate that electrolysis of a silver electrode in deionized water produces colloidal silver containing both metallic silver particles (1-25 wt%) and silver ions (75-99 wt%). The silver particles observed in colloidal silver generally range in size from 5 to 200 nm. This information suggests – but certainly does not conclusively prove – that the SilverCare™ washing machine discharges a mixture of silver ions and silver nanoparticles.

2. Dilution

Wash cycle uses 12.68 gal water [11]

Typical residence generates 70 gallons wastewater per person per day [12]

Unknowns:

- Number of people in community?

- Number of SilverCare™ washing machines in community?

- Amount of laundry per person per day?

- Other sources of non-domestic wastewater in community?

3. Transformation

Unknowns:

- Samsung: "silver sticks to the fabric" [8]

- Sorption to other solids?

- Agglomeration?

- Chemical/biological reactions?

4. Output

Estimated [Ag] (ug/L) for May 2006, calculated as follows:

- Maximum estimate is an extreme upper bound estimate.

- Minimum does not reflect all sources of dilution, thus is a conservative estimate.

5. Effects

Acute ambient water quality criterion (not nano-specific) 3.2 ug/L [12].

Few experiments have tested the toxicity of nano Ag at relevant concentrations. Existing data show potential for toxicity but are not conclusive.

Table 1: Toxicity Tests on Silver Nanoparticles

<table>
<thead>
<tr>
<th>Ag Solutions</th>
<th>Effect on Bacterial Growth</th>
<th>Effect on Fish</th>
<th>Effect on Aquatic Ecosystems</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 ug/L nano Ag (15 nm)</td>
<td>Cell viability and proliferation</td>
<td>Toxic to E. coli.</td>
<td>Toxic to aquatic life, dependent wildlife, human health, and the potential for exposure, nanomaterials may be regulated under the CWA. [4]</td>
</tr>
<tr>
<td>1000 µg/L nano Ag (14.6 nm)</td>
<td>Cell viability and proliferation</td>
<td>Toxic to E. coli.</td>
<td>Toxic to aquatic life, dependent wildlife, human health, and the potential for exposure, nanomaterials may be regulated under the CWA. [4]</td>
</tr>
<tr>
<td>2500 µg/L nano Ag (18.5 nm)</td>
<td>Cell viability and proliferation</td>
<td>Toxic to E. coli.</td>
<td>Toxic to aquatic life, dependent wildlife, human health, and the potential for exposure, nanomaterials may be regulated under the CWA. [4]</td>
</tr>
<tr>
<td>5000 µg/L nano Ag (12.3 nm)</td>
<td>Cell viability and proliferation</td>
<td>Toxic to E. coli.</td>
<td>Toxic to aquatic life, dependent wildlife, human health, and the potential for exposure, nanomaterials may be regulated under the CWA. [4]</td>
</tr>
<tr>
<td>10000 µg/L nano Ag (9.1 nm)</td>
<td>Cell viability and proliferation</td>
<td>Toxic to E. coli.</td>
<td>Toxic to aquatic life, dependent wildlife, human health, and the potential for exposure, nanomaterials may be regulated under the CWA. [4]</td>
</tr>
</tbody>
</table>

Inhibitory Effects of Silver on Microbial Growth

Decrease in Bacterial Counts (cells/mL)

Flanobacterium sp.

Conclusions
As the commercialization of nanoscale materials grows, and the consumer use of products containing nanoparticles increases, so will the discharge of nanomaterials to wastewater treatment plants. Limited data are available to estimate such discharges. While the CWA protects against toxic discharges, the uncertainty surrounding the possible effects of nanoscale materials may prompt the need to adapt controls on some products. EPA is considering how best to address these issues, but little information is available publicly.

Interested parties should monitor the technical literature and regulatory and legislative developments in this regard. Novel technologies require novel solutions and the interests of nanotechnology are best served by ensuring that nanoscale materials are managed prudently, thoughtfully, and carefully. Perhaps the best and most immediate defense against a potential consumer backlash is a good dose of precaution, the use of Life Cycle Analysis to evaluate end-of-life impacts, and an enduring commitment to product stewardship and environmental protection. And, as with any emerging environmental issue, clear, timely, and accurate communication with the public and other stakeholders goes a long way in distinguishing between perception and reality.

Please see hand out for list of references.