Outline of Presentation

1. Objectives
2. Nitrification Process
3. Pilot Scale WWTP
4. Full Scale WWTP
5. Conclusions
Silver may enter and affect receiving waters by point sources.

Who cares on Silver Release and Pathways to Water?

Michael Burkhardt, BfR, Berlin
Who cares on Products and Amounts - What's “nanosilver”?*

- In Europe <50 t/a particulate silver in use, <4 t/a Ag for textiles (90% AgCl)
- 30% of all nano-projects dealing with “nanosilver” (Maynard 2006)

<table>
<thead>
<tr>
<th>Silver Form</th>
<th>Silver Ion Exchange</th>
<th>Silver Salt</th>
<th>Metallic Silver</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium Phosphate</td>
<td>Ion</td>
<td>20 - 500</td>
<td>Metallic Microcomposite Silver</td>
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<tr>
<td>Zeolithe</td>
<td>Ion</td>
<td>20 - 500</td>
<td>Metallic Nanosilver</td>
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<tr>
<td>Silver Glass</td>
<td>Ion</td>
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<tr>
<td>Silver Polymer</td>
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<tr>
<td>Microcomposite Silver Chloride</td>
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<tr>
<td>Silver Chloride</td>
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<tr>
<td>Metallic Silver</td>
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<table>
<thead>
<tr>
<th>Size (nm)</th>
<th>Ion</th>
<th>Ion</th>
<th>Ion</th>
<th>Ion</th>
<th>5 - 25</th>
<th>5 - 25</th>
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<table>
<thead>
<tr>
<th>Matrix</th>
<th>Exchange Resin</th>
<th>Alumo Silicate</th>
<th>Phosphate Glass</th>
<th>Polymer</th>
<th>Titanium Dioxide, Zeolithe</th>
<th>Amorphous Silicate</th>
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<tbody>
<tr>
<td>Size (nm)</td>
<td>&gt;1000</td>
<td>&gt;1000</td>
<td>&gt;1000</td>
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<td>-</td>
<td>&gt;1000</td>
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<th>Dosage Form</th>
<th>granular</th>
<th>granular</th>
<th>liquid</th>
<th>liquid</th>
<th>granular</th>
<th>liquid</th>
<th>liquid, granular</th>
<th>liquid</th>
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</thead>
</table>

Goal of the Study: Behavior of Silver in Wastewater

- Influence on nitrification in activated sludge
  (silver chloride, metallic nanosilver, metallic microcomposite silver)

- Mass balance in a pilot WWTP with 70 equivalent inhabitants
  (silver chloride, metallic nanosilver)

- Mass balance in a full-scale WWTP with 60'000 equivalent inhabitants
  (including silver discharge by laundry)

Test conditions represent “real world” (composition matrix) and analytical methods are state-of-the-art for environmental samples
Outline of Presentation

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Nitrification Inhibition Test with Real Activated Sludge

Aerated batch reactors operated with 3 L activated sludge

- Addition of four silver products
  - 1 mg/L Silver, corresponding to 250 mg Silver / Dry Matter
  - 100 mg/L Silver, corresponding to 25'000 mg Silver / Dry Matter
- Exposure time to silver 2 hours and 6 days
- Addition of ammonium and oxidation within 2 hours measured
- Reactors without silver for each product as reference

Addition Silver

- 20 mg/L \(NH_4-N\)

Reference (without silver)

- 20 mg/L \(NH_4-N\)

3 L Batch reactors, Temperature +20°C
## Tested Silver Forms (Market Products)

<table>
<thead>
<tr>
<th>Silver Forms</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver nitrate (Reference)</td>
<td>AgNO₃</td>
</tr>
<tr>
<td>Silver Chloride</td>
<td>AgCl</td>
</tr>
<tr>
<td>Metallic Nanosilver A</td>
<td>nAg-A</td>
</tr>
<tr>
<td>Metallic Nanosilver B</td>
<td>nAg-B</td>
</tr>
<tr>
<td>Metallic Microcomposite Silver</td>
<td>Micro</td>
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</tbody>
</table>

* Similar to JRC NM-300 K

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Nitrification Results of 1 mg/L Silver Addition

Concentration of 250 mg Ag /kg DM represents “worst-case”
(even higher than by discharge of photochemistry in the past)
Nitrification Results of 100 mg/L Silver Addition

Conditions reflecting our scientific interest in processes (25 g Ag /kg TS overburdened the test system)
Outline of Presentation

1. Objectives
2. Nitrification Process
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5. Conclusions
Plant operated under conditions similar to full-scale WWTP
- Inflow 1 m³/h wastewater directly from combined sewer system
- Activated sludge with 12 days age and 3 g/L dry matter (DM)

Addition of “nanosilver A (nAg-A)” and “silver chloride (AgCl)” (25 days)
- 2400 µg/L Ag for 1 day (pulse for rapid equilibrium)
- 200 µg/L Ag for 24 days (continuous)
- Sampling of effluent and sludge
Addition of silver using pump

Effluent of secondary clarifier
Silver Concentration in Effluent and Sludge

- Initial Pulse Addition (2400 µg/L Ag)
- Continuous Addition (200 µg/L Ag)

**Effluent**

**Sludge**

Silver Addition

- Silver Addition (µg/L)
- Recovery Time

Silver in Effluent (µg/L)

Silver in Sludge (µg/L)

Time (d)
Excellent elimination of particulate silver in WWTP
Mass Balance of Silver in Pilot WWTP

Silver chloride addition (iSysAG)
- Sludge: 96%
- Effluent: 4%

Nanosilver addition (NM-K 300)
- Sludge: 93%
- Effluent: 6%
- Not Detected: 1%

Strong correlation to suspended solids (dry matter)
Silver Particles attached to Activated Sludge Flocs

After Addition of Nanosilver A (NM-K 300)
Silver Particles attached to Flocs in Effluent Water

After Addition of Nanosilver A (NM-K 300)
Technology for Tertiary Treatment

Drum filtration (10 µm)

<table>
<thead>
<tr>
<th>Days</th>
<th>Silver</th>
<th>DM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>20</td>
</tr>
</tbody>
</table>

Similar barrier as sand filter

Michael Burkhardt, BfR, Berlin
Silver Speciation using EDX

After addition of silver chloride

Rapid silver transformation to silver sulfide in real wastewater
1. Objectives
2. Nitrification Process
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Silver Mass Flow in Full Scale WWTP

Kloten/Opfikon for 60'000 inhabitant equivalent
Sampling Scheme in WWTP

Influent

Bar Screen
Settling Tank
Primary Treatment

Opfikon *
Kloten

+ Digested Sludge

Secondary Treatment (Nitrification)

Secondary Clarifier
Biology

Tertiary Treatment (Sand filter)

Secondary Clarifier
Biology

Receiving Water

Effluent

* Discharge of silver from an industrial laundry using AgCl. Application stopped completely 2010.
### Mass Flow of Silver in WWTP

#### Daily composite samples of dry weather flow

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inflow (μg Ag /L)</th>
<th>Outflow (μg Ag /L)</th>
<th>Elimination (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Opfikon*</td>
<td>Kloten**</td>
<td>Effluent</td>
</tr>
<tr>
<td>1</td>
<td>14.0</td>
<td>1.9</td>
<td>0.54</td>
</tr>
<tr>
<td>2</td>
<td>18.4</td>
<td>1.6</td>
<td>0.19</td>
</tr>
<tr>
<td>3</td>
<td>12.3</td>
<td>5.3</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>12.3</td>
<td>2.5</td>
<td>0.07</td>
</tr>
</tbody>
</table>

* Worst-case related to industrial laundry (application stopped 2010)
** Corresponding with background concentration

* Silver present as silver sulfide
Outline of Presentation

1. Objectives
2. Transfer Pathways
3. Sources
4. Fate
5. Conclusions
Conclusions to Nanosilver / Particulate Silver

**Emission**
- Small amounts release to wastewater (e.g. from coating, laundry)
- Low influent concentrations of WWTP (even under worst-case conditions)
- Occurrence mainly as AgS attached to larger particles

**Fate in WWTP**
- No effect on nitrification process (microbial activity not inhibited)
- Excellent elimination (95-99%) which is similar to CeO and TiO₂
  (in Switzerland micropollutants elimination >80% in the future)
- Attached to sludge flocs (thus filtration possible)
- Rapid transformation to insoluble AgS

**General remark**
- Testing under artificial laboratory conditions (matrix, concentration, coating)
  gives limited insight to environmental behavior (but to processes)
- Up-to-date testing, sampling, analysis are required (chemical, physical, visual)
Adsorption at Air–Water Interfaces

Handle nanosilver with care (e.g. Influence on recovery)
Reduction of AgCl to Ag⁰ by Electron Beam (SEM)

Handle AgCl with care in tests
Acknowledgements

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n Eawag (Swiss Federal Institute of Aquatic Science and Technology)

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Literature

n Zuleeg et al. (2009): Charakterisierung und Bilanzierung von Silberpartikeln in Abwasserreinigungsanlagen. BAFU-Bericht, 29 S.


Thank you for Attention!