Effect of different water conditions on dissolution of nanosilver
Shao-Feng Chen, Hongyin Zhang and Qing-Yu Lin

ABSTRACT
This study evaluates the time-dependent dissolution of nanosilver (nAg) in common electrolytes and natural waters. nAg was synthesized via Tollens’ method using sodium citrate as stabilizer; its morphology, UV–Vis spectrum, and particle size were characterized. The dissolved silver was monitored over time using filtration, centrifugation, and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Our results indicated that nanoparticle aggregation, Cl⁻/C₀ presence, and natural organic compounds could affect the dissolution behavior of nAg. The dissolution of nAg was highly dependent on Cl⁻/C₀ concentration. Excessive Cl⁻ enhanced nanoparticle dissolution, whereas natural organic compound inhibited the dissolution. The dissolution data fitted well with the first-order kinetic model, and the dissolution rate coefficients were calculated using the first-order equation. This study showed the dissolution of nAg under various water conditions. The obtained results may be helpful in predicting nAg behavior in relevant environmental aquatic systems.

INTRODUCTION
Nanotechnology has developed rapidly in recent years. Nanomaterials have been extensively applied in industries and households, among which nanosilver (nAg) is one of the most widely used, as documented by nanotechproject.com (2011). nAg is incorporated into consumer and medical products as a broad-spectrum antimicrobial agent (Jin et al. 2010; Liu et al. 2010). Therefore, nAg can be released into sewage or natural water bodies because many products release nAg through washing, abrasion, or disposal (Colvin 2003). Released nAg can cause negative environmental effects by harming naturally occurring microorganisms, such as bacteria and protozoa, due to its antimicrobial properties (Sondi & Salopek-Sondi 2004; Choi & Hu 2009; Choi et al. 2009; Elzey & Grassian 2009; Gao et al. 2009; Rai et al. 2009; Sharma et al. 2009; Jeong et al. 2012). The toxicity of nAg is mainly attributed to dissolved Ag⁺ (Chen & Zhang 2013; Jin et al. 2010; Zook et al. 2011; Jeong et al. 2012). In addition, the proposed antimicrobial mechanism suggests that dissolved Ag⁺ adsors on or penetrates into the cell membrane, disturbs the thiol groups on proteins or DNA, and causes cell death (Rai et al. 2009; Sharma et al. 2009). Environmental factors such as ionic strength, presence of specific ions, pH, or natural organic compounds can affect nAg dissolution, thereby influencing its toxicity in environmental conditions (Liu & Hurt 2010; Liu et al. 2010; Li & Lenhart 2012; Zhang & Chen 2012). Prior studies have investigated the dissolution of nAg with different particle sizes and coating agents, as well as under different temperatures, ionic strengths, and oxygen contents in solutions (Liu & Hurt 2010; Liu et al. 2010; Li & Lenhart 2012). To the best of our knowledge, studies on the effect of natural waters and different water compositions on nAg dissolution are still rare (Li & Lenhart 2012).

In this work, NaCl and CaCl₂ were chosen as electrolytes because Na⁺, Ca²⁺, and Cl⁻ are the most abundant cations and anions in natural waters. Humic acid (HA) solution was used to mimic the natural organic compounds present in natural waters. Lake water, groundwater, and seawater were used as typical natural water conditions. nAg was prepared through Tollens' method, using sodium citrate as stabilizer. The dissolution of nAg was monitored using these synthetic and natural water conditions.

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EXPERIMENTAL

Tollens’ method applies saccharides to reduce the Ag \((\text{NH}_3)_2\)\(^+\) complex into elemental silver. In our work, Ag \((\text{NH}_3)_2\)\(^+\) was reduced by maltose, and the pH of the solution was adjusted to 10 using NaOH. Sodium citrate was used as stabilizer because of its extensive use in previous studies (Huynh & Chen 2011; Chen & Zhang 2012; Li et al. 2012). NaCl and CaCl\(_2\) solutions were used because the ions Na\(^+\), Ca\(^{2+}\), and Cl\(^-\) represent the most abundant cations and anions in common natural water conditions. Table 1 shows the concentrations of the electrolytes used in this study. Humic acid (Sigma–Aldrich) was used to mimic the natural organic matter in natural waters. Lake water, groundwater, and seawater samples were collected in Songshan Lake, Maoming City, and Jinxing Bay, respectively. The ions in natural waters were determined by ion chromatography (Dionex, ICS-5000). Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, TOC-VWS). The ionic concentration and natural organic matter content of the natural water samples are listed in Table 2.

Characterization of the obtained nAg was conducted using a UV–Vis spectrometer (Genesys, Thermo Scientific) and transmission electron microscopy (TEM) (JEM-2100, Jeol). The dynamic light scattering technique was used to measure the particle size of nAg using a zetasizer (NanoZS, ZEN 360, Malvern).

A dissolution kinetics experiment was conducted by adding the obtained nAg into different water samples (final nAg concentration: 1 mg/L). The solutions were then stored in a rotating incubator at 25 \(^\circ\)C. The dissolved silver was measured as total silver using a previously described method with minor modifications (Elzey & Grassian 2009). In brief, the nAg solutions were passed through a 0.22 \(\mu\)m filtration membrane and centrifuged for 45 min at 13,000 rpm to separate nAg with Ag\(^+\). The supernatant was decanted and measured by inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Elemental). The obtained data were fitted using a first-order kinetic equation modified from Kittler et al. (2010):

\[
y = b - a e^{-kt}
\]

where \(y\) is the dissolved Ag\(^+\) at time \(t\); \(t\) is the elapsed time; \(b\) is the final concentration of the released Ag\(^+\); \(k\) is the dissolution rate coefficient; and \(a\) is the fitted coefficient at the electrolyte concentration applied.

RESULTS AND DISCUSSION

Characterization of nAg

Figure 1 presents the UV–Vis spectroscopic and TEM characterization of the obtained nAg. The UV–Vis spectrum showed that the nAg peak is located at 408 nm, which is consistent with other studies (Kvitek et al. 2008; Liu & Hurt 2010). The TEM image shows that the obtained nAg is near spherical.

Particle size of nAg in synthetic aqueous solutions and natural waters

The particle size of nAg in electrolyte solutions indicates that high ionic strength could induce nAg aggregation (Figure 2). Our result is consistent with other studies (Huynh & Chen 2011; Li & Lenhart 2012). The observed aggregation behavior

Table 1 | Compositions of electrolyte and humic acid in the synthetic aqueous solutions

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Concentrations</th>
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<tbody>
<tr>
<td>NaCl</td>
<td>0.1 mmol/L</td>
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<td></td>
<td>1 mmol/L</td>
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<td></td>
<td>10 mmol/L</td>
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<td></td>
<td>100 mmol/L</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>0.1 mmol/L</td>
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<tr>
<td></td>
<td>1 mmol/L</td>
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<tr>
<td></td>
<td>10 mmol/L</td>
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<tr>
<td></td>
<td>100 mmol/L</td>
</tr>
<tr>
<td>HA</td>
<td>1 mg/L as TOC</td>
</tr>
<tr>
<td></td>
<td>2 mg/L as TOC</td>
</tr>
<tr>
<td></td>
<td>10 mg/L as TOC</td>
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</table>
agrees with the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. At low concentrations of NaCl, an increase in electrolyte concentration elevates the screening of nAg surface charges, thereby reducing the energy barrier between the nanoparticles. At high electrolyte concentrations, the nAg charges are completely screened and the energy barrier against aggregation is removed (Li et al. 2010; Huynh & Chen 2011). In addition, divalent cation Ca\(^{2+}\) has been observed to enhance nAg aggregation more effectively, in agreement with the Shulze–Hardy rule which indicates that the stability of a nanosuspension is extremely sensitive to the valence of the counterions present in the suspension (Jin et al. 2010). In our study, given that the nAg surface is negatively charged (zeta potential measured by zetasizer: \(-35\) mV), the valence of the cations present in the suspension has an important role in screening the negative surface charges on nAg. Figure 2(b) does not show significant changes in the particle sizes in HA solutions because the HA molecules could be adsorbed onto the nAg surface and create steric repulsion between nanoparticles (Huynh & Chen 2011; Chen & Zhang 2012). In Figure 2(c), the particle size of nAg in seawater is much larger than those in
groundwater and lake water due to high ionic strength and concentrations of divalent cations (Table 2). The result also agrees with previous literature (Gao et al. 2009; Chinnapongse et al. 2011).

**Dissolution of nAg in synthetic aqueous solutions**

Figure 3 shows the dissolution experiments. The proposed mechanism of the dissolution of nAg is surface oxidation by dissolved oxygen (Zhang et al. 2011):

\[
\text{Ag(s)} + 1/4\text{O}_2 + \text{H}^+ \leftrightarrow 2\text{Ag}^+ + \text{H}_2\text{O}
\]  

As the released Ag\(^+\) reaches a certain concentration, the reaction could reach equilibrium (Liu & Hurt 2010).

In aqueous solutions with Cl\(^-\), dissolved Ag\(^+\) reacts with Cl\(^-\) and forms AgCl precipitate, which decreases the measured dissolved silver (Figure 3). However, high concentration of Cl\(^-\) can dissolve AgCl by forming the soluble silver chloride complexes AgCl\(_2\) and AgCl\(_3\), resulting in high concentration of dissolved silver (Liu & Hurt 2010; Liu et al. 2010). The aforementioned reactions explain the dissolution behavior observed in our experiment, where increased Cl\(^-\) reduces the dissolved silver concentration due to the generation of insoluble AgCl. In addition, the nAg dissolution was enhanced by excessive Cl\(^-\) due to the formation of soluble silver chloride complexes. A similar dissolution behavior was observed in the CaCl\(_2\) solution. Compared with the nAg dissolution in 100 mmol/L NaCl solution, nAg in 100 mmol/L CaCl\(_2\) produced more soluble silver (Figure 3) after 5 days of incubation. This result is attributed to higher Cl\(^-\) concentration in the CaCl\(_2\) solution (Table 1).

However, the dissolved silver was less in the CaCl\(_2\) solutions compared with that in NaCl. Considering that Ca\(^{2+}\) produces nAg aggregates more effectively, the aggregation of nAg can significantly reduce its surface area, thereby inhibiting surface oxidation. Notably, both the aggregation behavior and the presence of Cl\(^-\) in the aqueous solutions affected nAg dissolution. However, in our study, the two factors are not contradictory. High concentration of Cl\(^-\) enhances nAg dissolution, thereby reducing the size of individual nanoparticles. However, the aggregation behavior is not only associated with the individual nanoparticle size, but also with the number of nanoparticles.

Figure 3(c) presents the dissolution of nAg in the HA solution. HA inhibits nAg dissolution in a dose-dependent manner. Contrary to the dissolution behavior in electrolyte solutions, the concentration of dissolved silver in the HA solution decreased over time. Studies have suggested that the adsorption of HA molecules can block nAg oxidation sites (Dubas & Pimpan 2008; Gao et al. 2009). Another mechanism proposed that released Ag\(^+\) can be reduced to nAg via the reducing sites on HA molecules (Sal’nikov et al. 2009).
Table 3 shows the dissolution rate coefficient $k$ ($d^{-1}$) calculated from the first-order kinetic equation. The first-order kinetic model fitted well with the experimental data with correlation coefficients of 0.909 to 0.999. Consistent with our aforementioned discussion, dissolution rate coefficients of nAg in CaCl₂ (0.40 to 0.79) and HA solutions (0.72 to 0.82) are lower than those in NaCl (1.01 to 2.28) due to the aggregation behavior caused by Ca²⁺ and the adsorption behavior of HA molecules.

**Dissolution of nAg in natural water conditions**

In natural water conditions, seawater produced the highest concentration of dissolved silver (Figure 4). This observation is consistent with previous results which show that high concentration of Cl⁻ could form soluble silver chloride complexes (Liu et al. 2010). Lake water is rich in natural organic matter (8.4 mg/L as TOC). Similar to HA, the natural organic matter can either adsorb onto the surface of nanoparticles to prevent nAg dissolution or act as a reductant to reduce Ag⁺ to nAg. Similarly, Gao et al. (2009) found more dissolved silver of nAg in seawater (0.66 mg/L) than in river water rich in natural organic matter (0.043 mg/L) (Gao et al. 2009). The dissolution rate coefficients in natural waters (Table 3) show that nAg dissolves faster in seawater than in groundwater and lake water. As described in the previous section, this phenomenon is ascribed to the presence of high Cl⁻ concentration (Table 2), which could enhance nAg dissolution.

**CONCLUSION**

In this work, the dissolution behavior of nAg under various water chemistry conditions was determined. Our results showed that the presence of Cl⁻ in the aqueous solution has significant effects on nAg dissolution. Low concentration of Cl⁻ inhibits nAg dissolution, whereas excessive Cl⁻ enhances generation of soluble silver species. In addition, the aggregation of nAg and the presence of HA molecules can reduce nAg dissolution. In natural water conditions, our results indicated a high level of nAg dissolution in seawater, whereas natural organic compounds may inhibit the dissolution in lake water. This article may explain the dissolution behavior of nAg under different water chemistry conditions. However, future model simulations involving more environmental factors, such as pH and dissolved oxygen, as well as the characteristics of nAg, such as particle size and coating materials, are warranted.

**REFERENCES**


Sondi, I. & Salopek-Sondi, B. 2004 Silver nanoparticles as antimicrobial agent: a case study on, E. coli as a model for gram-negative bacteria. J. Colloid Interface Sci. 275 (1), 177–182.


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