The Behavior of Silver Nanotextiles during Washing

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The widespread use of silver nanoparticles (Ag-NPs) in commercial products, especially textiles, will likely result in an unknown spread of Ag into the environment. The quantification and characterization of the Ag released from nano-Ag-products is an important parameter needed to predict the effect of Ag-NPs on the environment. The aim of this study was to determine the amount and the form of Ag released during washing from nine fabrics with different ways of silver incorporation into or onto the fibers. The effect of pH, surfactants, and oxidizing agents was evaluated. The results show that little dissolution of Ag-NPs occurs under conditions relevant to washing (pH 10) with dissolved concentrations 10 times lower than at pH 7. However, bleaching agents such as hydrogen peroxide or peracetic acid (formed by the perborate/TAED system) can greatly accelerate the dissolution of Ag. The amount and form of Ag released from the fabrics as ionic and particulate Ag depended on the type of Ag-incorporation into the textile. The percentage of the total silver emitted during one washing of the textiles varied considerably among products (from less than 1 to 45%). In the washing machine the majority of the Ag (at least 50% but mostly >75%) was released in the size fraction >450 nm, indicating the dominant role of mechanical stress. A conventional silver textile did not show any significant difference in the size distribution of the released silver compared to many of the textiles containing nano-Ag. These results have important implications for the risk assessment of Ag-textiles and also for environmental fate studies of nano-Ag, because they show that under conditions relevant to washing, primarily coarse Ag-containing particles are released.

Introduction

The use of silver or silver nanoparticles (Ag-NPs) in commercial products is proliferating and thus it is expected that the environment will be increasingly exposed to these materials. Ag-NPs are one of the most promising NPs for future applications due to their antimicrobial, antifungal, and partially antiviral properties (*1*). During use the Ag-NPs slowly dissolve, releasing dissolved Ag^+ that is one of the most toxic metals for microorganisms (*2*). It is still unclear whether the toxicity of Ag-NPs is only due to dissolved Ag or if the Ag-NPs themselves also show a toxic effect (*3*). A modeling study has shown that biocidal plastics and textiles

can contribute up to 15% to the total Ag flow into the environment (*4*). Based on a life-cycle perspective of nano-products, environmental concentrations of Ag-NPs in natural waters of about 0.03 $\mu g\ L^{-1}$ were predicted (*5*).

Unfortunately, precise estimations of the emissions emanating from silver-containing materials are hampered by a lack of available information about the content and form of the silver in the products and their release. Assessing the risks posed in particular by the use of nanomaterials in commercial products requires a better understanding of the materials' mobility, bioavailability, and toxicity in the environment, which are strongly linked to the properties of the particles as they are actually released (*6*). Some data are available on the release of ionic Ag^+ from polymers containing Ag-NPs, but not about the release of particulate Ag (*7, 8*). A textile that is disposed at the end of its use phase has lost about 10% of its weight through abrasion during washing and usage (*9*), which suggests that particulate release may play a dominant role. One of the few available studies about NP release from products investigated the leaching of Ag-NPs from six brands of nanosocks into water (*10*). In that study, the socks were immersed in pure or tap water under shaking conditions for one or 24 h. At least three consecutive washes were conducted and the Ag was size fractionated. The wash solutions were also characterized by ion selective electrode measurements for ionic Ag^+ and by TEM/EDX analysis for particulate silver. The results suggest that both ionic and particulate Ag may be released from textiles during exposure to water.

The chemical conditions in natural water are very different from those during washing where high concentrations of surfactants are present and the pH is between 10 and 11. In addition, the use of bleaching agents, most notably H_2O_2 and peracetic acid (PAA) formed by the perborate/ TAED system (*11, 12*) can greatly influence the release of Ag^+ because metallic Ag needs to be oxidized in order to release ionic Ag^+. Experiments under such conditions are decisive in representing the "real" washing conditions where the mechanical stress on the textiles also needs to be considered.

The aim of this work was to investigate the behavior of various silver-containing fabrics under conditions relevant for washing. The quantity and the form of Ag released (particulate or ionic) into the washing solution was determined by immersing the textile into a solution of pH 10 and by washing for 30 min at 40 °C. The influence of pH, surfactants, and oxidizing agents on Ag-NP dissolution and release from textiles was evaluated.

Materials and Methods

Materials. Nine different textiles were studied (Table 1). One sample was a commercially available conventional antibacterial sock (X-STATIC), one a commercially available nanosock (AgKilBact), six were fabrics obtained directly from two companies, and one was a sample from an ongoing research project (PLASMA-NP) (*13*). In order to determine the total Ag-content, three replicates of each textile were digested with 3.5 mL of HNO_3 (65%) and 1 mL of H_2O_2 (30%) (MLS 1200 MEGA digestion system, EM-45/A Exhaust Module). Silver was quantified by inductively coupled plasma optical emission spectroscopy (ICP - OES Perkin-Elmer OPTIMA 3000). Silver plasma standard solution (Specpure Ag 1000 μg/mL Ag in 5% HNO_3) from Alfa Aesar were used for calibration. For NP-PES and NP-PES-surf, containing the Ag inside a silica microsphere, the silver content in the samples was measured by X-ray fluorescence spectroscopy. NP-PES/PA was digested with 5 mL of HNO_3 (65%), 0.5 mL of H_2O_2 (30%)

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TABLE 1. Labeling, Description, Silver Incorporation, and Silver Content of the Fabrics Studied in This Work

textile label	description of textile	Ag-NP incorporation	silver content (mg/g)	RSD (%)
X-STATIC	79% cotton, 14% polyamide, 6% X-static fiber, 1% Lycra Elasthane	conventional textile: electrolytically deposited layer of Ag (several μm) on fiber	21.6	7.3
PLASMA-NP	polyester	plasma-coated fiber with Ag-NP (about 100 nm) embedded in PES matrix (*13*)	0.39	4.2
AgCl	cotton	AgCl ($\sim$200 nm) bound to the fiber surface	0.008	9.9
AgCl-BINDER	cotton	AgCl ($\sim$200 nm) incorporated in binder on the fiber surface	0.012	
NP-PES-SURF	polyester	Ag-NPs bound to the fiber surface	0.029	
NP-PES	polyester	Ag-NPs incorporated into PES fiber	0.099	
NP-PES/PA	80% polyester, 20% polyamide	Ag-NPs incorporated into fiber	0.242	
X-SYSTEMS	50% cotton, 39% Polyester, 6% Nylon, 5% Spandex	Ag-NPs incorporated inside the synthetic fibers (according to manufacturer)	0.003	31.5
AgKilBact	80% cotton, 20% Elastic Yarn	nanosized silver nanoparticles incorporated into cotton fibers (according to manufacturer)	2.66	0.4

and 0.5 mL of hydrofluoric acid (HF). Samples analyzed with HNO_3 digestions were also measured with XRF and HNO_3/HF digestion and the results were found to vary by not more than $\pm$ 20%.

Two types of Ag-NPs were employed in the experiments. One type, labeled "NP-powder" was obtained as powder from Auer-Remy GmbH (Hamburg, Germany). An aqueous suspension of Ag-NPs, labeled "NP-suspension" was obtained from NanoSys GmbH (Wolfhalden, Switzerland). A detailed characterization of particle and aggregate size of these carbonate-coated Ag-NPs is given in (*3*). The aggregate size of the silver nanoparticles in suspension under the conditions of the experiments was determined by LM 20 Nanosight with the software Nanosight NTA 1.5.1 The Ag-NPs were ultrasonicated for 5 min with an ultrasonication probe (BANDELIN Sonopuls Homogenizatoren HD 2070 - MS 7.3 mm − 70 W) at maximum power. The size distribution for suspensions of NP-powder and NP-suspension are shown in Supporting Information (SI) Figure S1. The average Ag-NP aggregate size for NP-powder was 104 nm $\pm$ 9 nm at pH 7 and 83 nm $\pm$ 7 nm at pH 10 in the presence of 0.1 g l^{-1} SDS. For the NP-suspension at pH 7 in the presence of 0.1 g l^{-1} SDS, the mean aggregate diameter was 37 nm $\pm$ 2 nm.

Analysis of Ag^+ with the Ion-Selective Electrode (ISE). The free Ag^+ ion concentration was measured using an Ag-ISE (Metrohm 6.0502.180) coupled with a Ag/AgCl reference electrode (Metrohm 6.0726.100) with double junction and potassium nitrate (KNO_3, 3 M) as the bridge electrolyte. Before each experiment a daily calibration curve was established from diluted $AgNO_3$ standard solutions prepared in the Ag^+ range from 1×10^{-3} to 1×10^{-6} M and extended to 7.96×10^{-8} M by means of NaCl addition. Visual-MINTEQ was utilized to calculate the resulting free Ag^+ concentration. The free ionic silver was 98.5 and 98.2% of the total dissolved silver at pH 7.1 and pH 10, respectively. The interference of the components used in the experiments (e.g., buffers, background ions, H_2O_2, perborate, TAED, surfactants) and pH on the ISE signal was tested with solutions of 10^{-5} M and 10^{-3} M Ag. In no case did the measured potential change by more than 2%. A complete loss of the free Ag^+ signal of the ISE was observed in the test washing powder. Silver standard solutions were prepared from silver nitrate ($AgNO_3$ 99.8%, Sigma-Aldrich) and were stored in the dark in order to prevent photoreduction. All solutions were prepared with nanopure water (16−18 MΩcm).

Dissolution of Ag-NPs. All measurements were carried out at room temperature in glass vessels protected from light in order to avoid photoreduction of silver. All suspensions were stirred at 100−150 rpm. Absorption of Ag on the glass walls was tested preparing a $AgNO_3$ standard solution of 9.3×10^{-7} M. After 50 min a decrease of the signal of less than 0.1 mV (<5.9%) was observed. $NaNO_3$ (0.03 M) was used to set the ionic strength and sodium carbonate (Na_2CO_3, 0.005 M) or MOPS (3-morpholino propane sulfonic acid, 0.01 M) were added to buffer the pH at 10 or 7. The Ag-NPs were added and the solution was ultrasonicated for 5 min at maximum power (70 W, BANDELIN Sonopuls HD 2070 - MS 7, 3 mm). The dissolution of the Ag-NPs was then followed over time recording the Ag^+ concentration using the ISE. The pH was also checked at the beginning and at the end of the experiments. 0.1 g/L SDS (n-dodecylsulfat sodium salt) or 0.1 g/L LAS (linear alkyl benzene sulfonate, MARLON AS 3, Sasol Germany GmbH) were added as surfactants. After 40−120 min the oxidizing agents H_2O_2 or peracetic acid (PAA) were added. They were titrated and standardized following the method described in (*14*). In some experiments the oxidants were produced in situ by the perborate/TAED system (N,N,N',N'-tetraacetylethylenediamine, TAED, 90%, and sodium perborate tetrahydrate).

The effect of H_2O_2 on the stability of Ag^+ was investigated at pH 10 by adding 0.002−0.04 mmol of H_2O_2 to 0.1 mM to 1 μM of silver standard solutions (in 0.1 g/L SDS and carbonate buffer). The Ag^+ concentration was followed over time using the ISE.

Release of Silver from Textiles: Influence of Oxidizing Agents and pH. The release of silver from textiles was studied at pH 10, buffered by 0.005 M Na_2CO_3 with SDS as surfactant (0.1 g/L). The textile samples were subjected to gentle agitation (stirring rate 100−150 rpm) and protected from light. The amount of fabric placed into solution ranged from 4.9 to 36.2 g L^{-1}. This large interval was due to the fact that some specimens had very low silver content and consistently more material was needed in order to detect silver in solution. The total silver introduced into the system varied from 1×10^{-6} to 1×10^{-3} M. After 120 min peracetic acid (PAA) was added. Similarly to the Ag-NP dissolution experiments, the ISE signal was recorded over time after placing the textiles in solution. In addition aliquots of the solution were taken for ICP-OES measurement with plastic syringes at different times. One aliquot of the solution was filtered using cellulose nitrate membrane filter (0.45 μm pore diameter, Sartorius), the other aliquot was used for total Ag analysis. These analyses were carried out in triplicate.

Release of Ag from Textiles during Washing. The washing procedure was conducted following an ISO-method for wash-tests (*15*) using a Washtec-P Roaches washing machine with

a motor speed of 40 ± 2 rpm, equipped with steel vessels with a capacity of 550 mL. Mechanical stress was exerted by 10 steel balls previously cleaned in HNO_3 (65%). Since the steel containers leached significant amounts of Ag, acid-cleaned HD-polyethylene bottles were placed inside them and completely surrounded by water to ensure heat transfer. The detergent/container volume ratio (0.279) (15) was kept the same as that in the steel vessel. The detergent was prepared dispersing $4 \, g \, L^{-1}$ ECE 98-standard washing powder (15) in distilled water (composition: 9.7% LAS, 5.2% nonionic surfactant, 3.6% soap, 4.5% antifoam, 32.5% zeolite, 11.8% carbonate, 5.2% acrylic acid, 3.4% Na-silicate, 1.3% CMC, 0.8% phosphonate, 9.8% sulfate, 12.2% others/water). The amount of textiles ranged from 4.7 to $27.4 \, g \, L^{-1}$, and the total silver introduced into the system varied from 1.9×10^{-6} to 1×10^{-3} M. The textiles were washed for 30 min at 40 °C. After washing, the fabrics were removed from the containers and rinsed with nanopure water for $1-2$ s before being wiped with soft tissues and let to dry before the next washing. For most fabrics a second wash was performed. In an additional washing cycle with new fabrics, perborate ($1 \, g \, L^{-1}$) and TAED ($0.15 \, g \, L^{-1}$) were added to the detergent immediately before the washing. From the detergent liquor a 15 mL aliquot was filtered with cellulose nitrate filter ($0.45 \, \mu m$, Whatman) and part of it further centrifuged through Amicon Ultra centrifugal filters (MW cutoff 30 kDa) for 10 min at $5000 g$ to obtain the dissolved fraction. Triplicate samples were analyzed by ICP-OES. The remaining detergent solution was homogenized by the ultrasonic probe for 2 min, and three replicates of 10 mL were taken and evaporated at 85 °C in an oven overnight. Following the addition of 1 mL HNO_3 (69%) and heating at 85 °C for $15-30$ min, the samples were diluted for ICP-OES measurements. We checked the repeatability of the washing procedure and found it to be $\pm 10\%$ for samples with high Ag-content and $\pm 20\%$ for samples with low Ag-content.

Preliminary tests were performed to assess any possible losses or contaminations of Ag during washing. In blank washings (no textile), but including filtering and ultrasonication, the silver signal was below the detection limit of ICP-OES. To account for the possible absorption on the steel balls or on HD-bottle walls, a similar test was performed spiking the detergent water with $0.9 \, \mu M$ Ag and measuring the concentration before and after a cycle. The recovery of Ag was 85%.

Results

Ag-NP Dissolution. The dissolution of the NP-powder and the NP-suspension at pH 7 in the presence or absence of surfactants is shown in Figure 1a. In the first phase without added oxidants a slight increase of the dissolved Ag^+ was measured over time. The presence of SDS decreased the concentration of released Ag^+. However, it has to be noted that in the absence of SDS the NP-powder did not form a suspension and only a few very large aggregates were present in the solution. No influence of SDS or LAS was observed on the dissolution of the carbonate-coated Ag-NPs. After addition of H_2O_2 a very rapid dissolution was observed with similar reactivity for both Ag-NPs. The final Ag^+/H_2O_2 ratio was 1.00 (NP-powder, no surfactant), 1.72 (NP-powder, SDS), 0.96 (NP-suspension, no surfactant), 1.23 (NP-suspension, SDS), and 1.82 (NP-suspension, LAS).

Figure 1b shows the dissolution of Ag-NPs at pH 10 with the addition of different oxidizing compounds. The Ag^+ signal in the first part without any oxidant present was at or below the detection limit of the ISE. The decrease of the signal is attributed to a slow equilibration of the electrode at very low Ag^+ concentrations. The dissolved Ag^+-concentration is at least a factor of 10 lower at pH 10 compared to pH 7. The addition of PAA resulted in almost immediate dissolution of the Ag-NPs. The addition of the same amount of H_2O_2 resulted
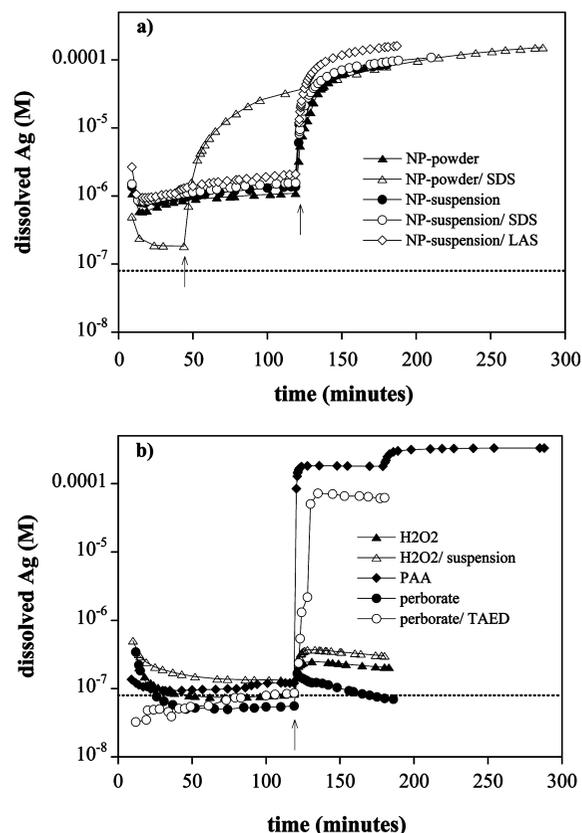
FIGURE 1. Dissolution of Ag-NPs at pH 7.1 (a) and pH 10 (b): the arrows indicate the time-point of H_2O_2 (0.088 mM) addition. The initial concentration of Ag in the experiments was 1.86×10^{-4} for the carbonate-coated Ag-NPs (NP-suspension) and varied from 9.09×10^{-4} to 9.72×10^{-4} for the NP-powder. All experiments were carried out at room temperature except perborate/ TAED at 40 °C. The dashed line indicates the detection limit of the ISE.

in a Ag^+ concentration that was 100-times lower. Perborate alone at 40 °C gave a small spike in dissolved Ag^+, followed by a gradual decrease in the signal. Perborate together with TAED at room temperature also resulted in a gradual increase in Ag^+ followed by a slow decrease over time. With higher perborate and TAED concentrations (equivalent to those during washing) and at elevated temperature, a rapid increase in Ag^+ was observed, followed by slight decrease after the peak.

The effect of H_2O_2 on the stability of Ag^+ at pH 10 is shown in SI Figure S2. Under all conditions the concentration of Ag^+ decreased after the addition of H_2O_2. The formation of a yellow-milky precipitate was clearly noticed at high Ag-concentrations. In the experiment with an excess of Ag^+ the ratio $Ag^+_{precipitated}/ H_2O_2$ was 1.4, indicating that each H_2O_2 was able to oxidize more than one Ag. XPS analysis of the precipitate showed that it is an Ag-oxide but the oxidation state of Ag could not be determined due to small differences between the peaks of the various species and inconclusive results from reference materials.

Silver Released from Textile Samples at pH 10. Figure 2 shows the evolution of Ag^+ over time after immersing the textiles at pH 10. In the first phase the textiles were exposed to the pH 10 solution for 120 min and then in the second phase the oxidant (0.1 mM PAA) was added, followed by a second addition of PAA (0.5 mM) 60 min later. Four out of the nine fabrics did not release any detectable Ag^+ (<0.08 μM) (AgCl-BINDER, NP-PES, NP-PES/PA, X-SYSTEMS). The other five samples exhibited very different behavior. AgKilBact released almost immediately a high concentration of Ag^+
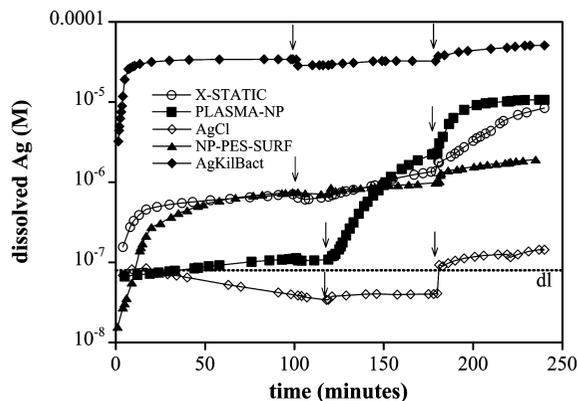
FIGURE 2. Ag⁺ release from textiles at pH 10 in the presence of SDS (0.1 g/L), with two additions of PAA (0.1 mM and 0.5 mM) after 120 and 180 min. For the other samples not shown in the figure (AgCl-BINDER, NP-PES, NP-PES/PA, X-SYSTEMS), the silver concentration was always below the detection limit (dashed line).
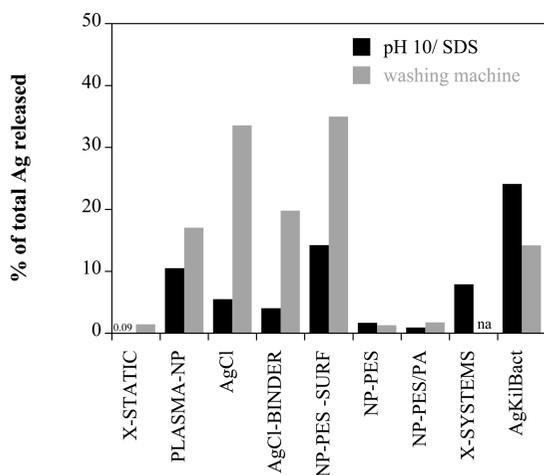
FIGURE 3. Silver released from the various textiles in pH 10/ 0.1 g l⁻¹ SDS solution (after 180 min) and during washing (30 min) in % of the total amount.

(about 25% of the total Ag), followed by a plateau and also the PAA addition did not yield big changes. Also X-STATIC and NP-PES-SURF released relatively rapidly Ag⁺, followed by a more gradual increase. PLASMA-NP released little Ag⁺ without oxidants but showed a rapid increase after both additions of PAA. The sample AgCl only gave a Ag⁺ concentration above the detection limit after the second addition of PAA.

Figure 3 shows with black bars the total Ag released after 150 min (after first PAA addition). The different samples leached between 0.09% (X-STATIC) and 24% (AgKilBact) of the total silver content within 150 min. In Figure 4a the distribution of the three fractions Ag⁺, particulate Ag smaller than 450 nm and particulate Ag larger than 450 nm is shown. The different textiles show very different behavior of silver release, whereas AgKilBact released almost all Ag in the dissolved form, NP-PES and X-Systems only released particulate Ag. The particulate fraction smaller 450 nm was found for four out of the nine fabrics: PLASMA-NP, AgCl, AgCl-BINDER, and NP-PES/PA. For X-STATIC and NP-PES-SURF dissolved and large particulate Ag was detected. The only major difference to the fractionation before PAA addition was observed for the sample PLASMA-NP where the fraction <450 nm was 80% (SI Figure S3).

However, when interpreting the results shown in Figure 4 it has to be noticed that due to the very low release of total Ag in some samples a value below the detection limit, e.g.,
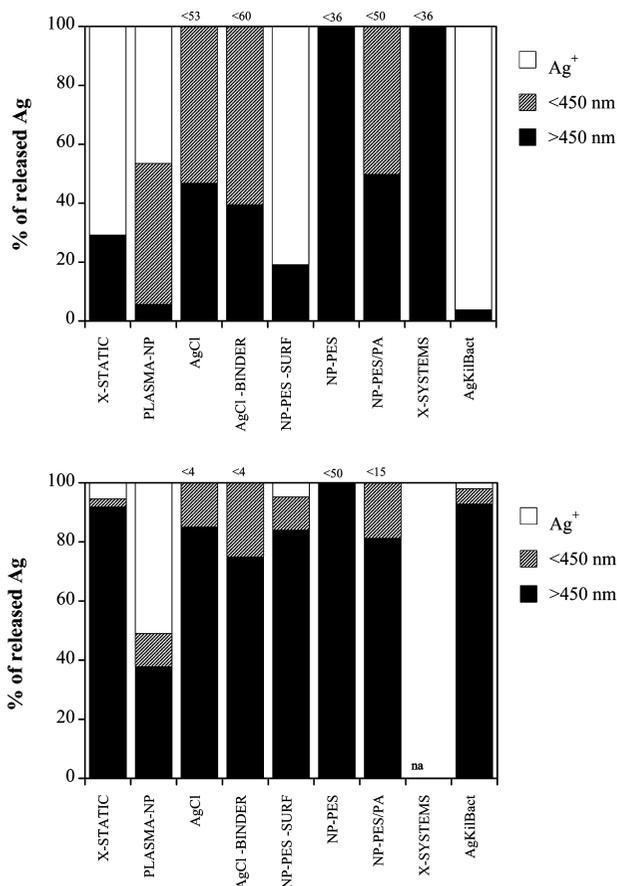
FIGURE 4. Fractionation of the silver released from the various textiles in pH 10/ 0.1 g L⁻¹ SDS solution (top) and during washing (first cycle, no bleach) (bottom).

TABLE 2. Release of Total Ag from Textiles During Washing in μg/ g of Textile

	1st cycle	2nd cycle	bleach cycle
X-STATIC	314	129	172
PLASMA-NP	67		
AgCl	2.7	1.8	3.6
AgCl-BINDER	2.4	0.9	3.2
NP-PES-SURF	10.1		
NP-PES	1.3	0.35	2.7
NP-PES/PA	4.3	1.6	10.2
AgKilBact	377	99	184

for the ion-selective electrode, could amount to a significant fraction of the total released silver. The concentration at the detection limit was converted for each fabric into the maximum silver fraction that could have been leached. The size fraction <450 nm, which was measured by ICP-OES having a lower detection limit than the ISE, could thus consist partially of dissolved Ag⁺.

Ag Released from Textiles during Washing. Figure 3 (gray bars) shows the percentage of the total Ag in the textile samples released into the washing solution after the first washing cycle without bleach. The total released Ag varied from 1.3 to 35% of the total Ag in the fabric. Table 2 shows the Ag released per gram of textile. The values vary by about a factor of 300 between the different textiles. Although X-STATC released only a small percentage of the total Ag, the absolute amount was very high. In contrast, the textiles with Ag incorporated into the fiber matrix released only very small amounts of Ag. For all the fabrics used the Ag release decreased in the second wash.

Figure 4b shows that the coarse Ag-fraction (>450 nm) was the most significant for most samples and ranged for all except one sample from 75 to 100% of the silver release. The PLASMA-NP sample differed from this behavior by having half of the Ag leached into the washing solution in the dissolved form. For the AgCl and the AgCl-BINDER samples no dissolved Ag was detected. The second wash or the addition of the bleaching agent did not change significantly the distribution of the Ag fractions (SI Figure S4 and S5).

Discussion

Seven out of the nine investigated fabrics contained zerovalent silver, and thus oxidation of Ag(0) to Ag(I) is a prerequisite for the appearance of Ag^+ in solution. Ag-NPs are extremely sensitive to oxygen and the chemisorbed Ag^+, either formed in air or during exposure to water, can be released once it comes into contact with water (16). The release of Ag^+ from Ag-NPs at pH 10, the pH during washing, is about $10 \times$ less than at pH 7. However, some of the textiles released in relatively short time large amounts of Ag^+ at pH 10, most notably AgKilBact, which leached 25% of the total Ag within minutes. It is probable that this freely leachable Ag was already present as Ag^+, maybe as a residue from synthesis. The remainder of the Ag was relatively inert with respect to dissolution. It is also possible that part or all of the Ag in this textile could be present in the form of a silver salt, e.g., as $AgNO_3$, which would also explain why it did not show an increased release after addition of the oxidant.

For most other textiles, a significant release of Ag^+ was only observed after addition of the oxidants. The main oxidants during washing are H_2O_2 and PAA, both formed in the perborate/TAED system. Perborate first dissociates to H_2O_2 which then reacts with TAED to form peracetic acid (PAA) which is a more active bleaching agent than hydrogen peroxide ($11, 12, 17$). H_2O_2 is able to oxidize metallic silver to Ag^+; a hydroxyl radical is also formed (18):

$$Ag(s) + H_2O_2 \rightarrow Ag^+(aq) + OH^{\cdot} + OH^-$$
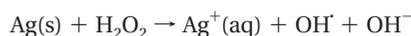
The hydroxyl radical can further oxidize metallic silver (19):

$$Ag(s) + OH^{\cdot} \rightarrow Ag^+(aq) + OH^-$$
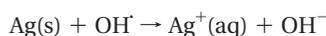
In the experiments at pH 7 the Ag^+/H_2O_2 ratio reached 1.73, indicating that the hydroxyl radical was indeed involved in the reaction. The ratio Ag^+/PAA that we observed at pH 10 was between 1.8 and 1.5, indicating that PAA oxidized Ag(0) in a similar reaction.

The decrease in Ag^+ after addition of H_2O_2 at pH 10 could be explained by a Fenton-like reaction of H_2O_2 with the Ag^+-ion and subsequent precipitation of Ag^{2+} as Ag(II)-oxide (20). Another possibility is the reduction of Ag^+ by H_2O_2 and formation of metallic Ag(0) (21). PAA, however, did not react with Ag^+ and no precipitate or disappearance of the Ag^+-signal was observed at pH 10 in the presence of PAA. In the perborate/TAED system (7.2/ 0.68 mM), both PAA and H_2O_2 are present at the same time and thus both rapid dissolution of Ag by PAA and precipitation of the formed Ag^+ by reaction with H_2O_2 occurred simultaneously, resulting first in an increase and later in a decrease of Ag^+ in solution depending on the kinetics of the formation of H_2O_2 and PAA from perborate and TAED and the kinetics of the reactions of both compounds with Ag and other components of the system (e.g., the textile fibers).

Large differences in the size distribution of the released Ag were found upon immersion in water. AgKilBact released almost all Ag in dissolved form, whereas NP-PES for example released Ag only in the size fraction >450 nm. This large variability of the size fractions is somewhat masked in the washing tests where the predominant fraction turned out to

be the largest size fraction, which is not surprising due to the mechanical damage produced by the steel balls in the test configuration. The way of Ag-NPs incorporation onto the fiber or into the polymer seemed to play a role only under gentle conditions.

The PLASMA-NP textile released Ag mainly in the particulate fraction passing the 450 nm filter, which was subsequently rapidly dissolved by PAA addition. Presumably this sample first released nanometer-sized particles containing silver which could then be rapidly oxidized by PAA. The AgCl and AgCl-BINDER textiles, where the Ag was present as AgCl particles, did not release any detectable dissolved Ag because of the high stability of the AgCl salt.

During washing the synergistic effects of chemical agents and the mechanical stress may enhance the Ag release from a textile. A comparison of the fabric samples indicates that the manufacturing processes play a determining role in the amount and form of Ag leached into wash water. The conventional Ag-textile X-STATIC did not show any significant differences in behavior compared to the Ag-NP textiles, except that it released much more Ag into solution. The addition of perborate and bleach activator did not seem to change significantly the relative percentage of the Ag-size classes or the amount of released Ag. This is surprising, given the huge influence that these compounds had in the tests performed at pH 10. It means that under "real-world" conditions during washing the effect of the oxidizing agents is masked, presumably by interactions of the oxidants with all the other components of the washing powder which thus lowers the available oxidant amount. The use of a washing powder containing bleach does not result in significantly higher Ag releases. The experiments with the NP-suspension showed that the presence of different surfactants at concentrations relevant to washing has only a small influence on the oxidative dissolution of Ag(0).

The amount of Ag leached from the socks found in our study (0.3–377 $\mu g/g$) is somewhat higher than the range reported by Benn and Westerhoff (1–68 $\mu g/g$) (10). This may be due to the fact that these authors only used distilled water and gentle agitation. However, the results of our study can not necessarily be considered representative for the whole lifetime of a textile because already the second cycle released less Ag. However, our first insight shows that Ag in the particulate fraction >450 nm is probably the predominant form of Ag released into the washing liquor and subsequently to wastewater. The composition and characterization of this coarse fraction, which could include Ag in fiber fragments, Ag-NPs aggregates or Ag precipitates, should be a focus in future research. The potential of chloride anions from tap water or the detergent formulation to precipitate Ag^+ as AgCl and thus to lower the amount of dissolved Ag should also be investigated. In addition the behavior of the coarse fraction during wastewater treatment or in the environment needs to be studied, especially if the Ag in this coarse fraction is dissolved or removed by wastewater treatment.

Supporting Information Available
Particle size distribution of the Ag-NPs. Effect of H_2O_2 on Ag^+ at pH 10. Size fractionation of Ag released from textiles at pH 10 after 100 min and in the 2nd and the bleach cycle of the

washing. This material is available free of charge via the Internet at http://pubs.acs.org.

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ES9018332