

University of Nebraska - Lincoln
DigitalCommons@University of Nebraska - Lincoln

U.S. Environmental Protection Agency Papers

U.S. Environmental Protection Agency

2014

Silver speciation and release in commercial antimicrobial textiles as influenced by washing

Enzo Lombi

University of South Australia, enzo.lombi@unisa.edu.au

Erica Donner

University of South Australia, CRC CARE

Kirk G. Scheckel

US Environmental Protection Agency

Ryo Sekine

University of South Australia

Christiane Lorenz

Technology and Society Laboratory, Gallen, Switzerland

See next page for additional authors

Follow this and additional works at: <http://digitalcommons.unl.edu/usepapapers>

Lombi, Enzo; Donner, Erica; Scheckel, Kirk G.; Sekine, Ryo; Lorenz, Christiane; and Von Goetz, Natalie, "Silver speciation and release in commercial antimicrobial textiles as influenced by washing" (2014). *U.S. Environmental Protection Agency Papers*. 216.
<http://digitalcommons.unl.edu/usepapapers/216>

This Article is brought to you for free and open access by the U.S. Environmental Protection Agency at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in U.S. Environmental Protection Agency Papers by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Authors

Enzo Lombi, Erica Donner, Kirk G. Scheckel, Ryo Sekine, Christiane Lorenz, and Natalie Von Goetz



Silver speciation and release in commercial antimicrobial textiles as influenced by washing



Enzo Lombi^{a,*}, Erica Donner^{a,b}, Kirk G. Scheckel^c, Ryo Sekine^a, Christiane Lorenz^{d,e}, Natalie Von Goetz^e, Bernd Nowack^d

^aCentre for Environmental Risk Assessment and Remediation, University of South Australia, Building X, Mawson Lakes Campus, South Australia 5095, Australia

^bCRC CARE, PO Box 486, Salisbury, South Australia 5106, Australia

^cNational Risk Management Research Laboratory, US Environmental Protection Agency, 5995 Centre Hill Avenue, Cincinnati, OH 45224, USA

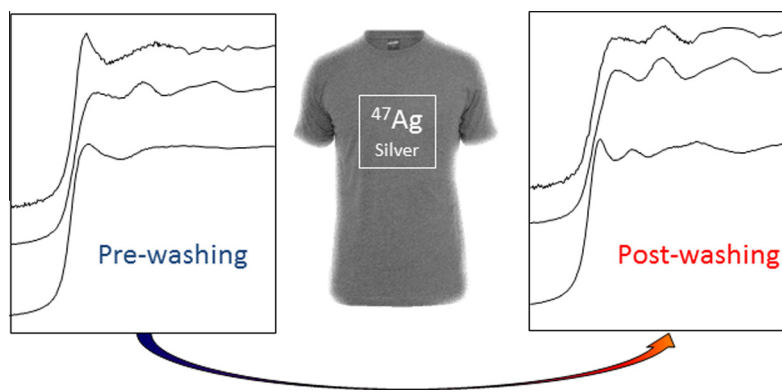
^dTechnology and Society Laboratory, Empa – Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, CH – 9014 St. Gallen, Switzerland

^eInstitute of Chemical and Bioengineering, ETH Zurich, Vladimir-Prelog-Weg 10, 8093 Zurich, Switzerland

HIGHLIGHTS

- The speciation of silver in commercial textiles, as revealed by XANES, is complex.
- Silver nanoparticles are only one of several Ag species in commercial textiles.
- Washing with two detergents resulted in significant changes in silver speciation.
- The complexity of Ag speciation in textiles complicates exposure assessment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 24 January 2014

Received in revised form 20 March 2014

Accepted 24 March 2014

Handling Editor: I. Cousins

Keywords:

Silver nanoparticles

Textiles

Washing

Speciation

ABSTRACT

The use of nanoscale Ag in textiles is one of the most often mentioned uses of nano-Ag. It has previously been shown that significant amounts of the Ag in the textiles are released upon washing. However, the form of Ag present in the textiles remains largely unknown as product labelling is insufficient. The aim of this study was therefore to investigate the solid phase speciation of Ag in original and washed silver textiles using XANES. The original Ag speciation in the textiles was found to vary greatly between different materials with Ag(0), AgCl, Ag₂S, Ag-phosphate, ionic Ag and other species identified. Furthermore, within the same textile a number of different species were found to coexist. This is likely due to a combination of factors such as the synthesis processes at industrial scale and the possible reaction of Ag with atmospheric gases. Washing with two different detergents resulted in marked changes in Ag-speciation. For some textiles the two detergents induced similar transformation, in other textiles they resulted in very different Ag species. This study demonstrates that in functional Ag textiles a variety of different Ag species coexist before and after washing. These results have important implications for the risk assessment of Ag textiles because they show that the metallic Ag is only one of the many silver species that need to be considered.

© 2014 Elsevier Ltd. All rights reserved.

* Corresponding author. Tel.: +61 8 8302 6267.

E-mail address: enzo.lombi@unisa.edu.au (E. Lombi).

1. Introduction

The functionalization of textiles such as cotton, wool and synthetic materials with Ag in order to impart antimicrobial properties to commercial products is an area of intense research and commercial growth (Radetic, 2013). In particular, the use of Ag nanoparticles (Ag-NPs) has been advocated for several reasons including the possibility to avoid discoloration, which occurs when ionic Ag is used (Vigneshwaran et al., 2007), negligible impact on fabric breathability and handling (Wong et al., 2006) and an overall smaller environmental impact (Windler et al., 2013). Due to the increased production of Ag functionalized textiles, these materials are one of the major sources of Ag-NPs release to the environment (Mueller and Nowack, 2008; Gottschalk et al., 2009; Arvidsson et al., 2011).

Only a few studies so far have investigated the speciation and release of Ag from Ag-functionalized commercial products. The amount of Ag released, as well as the percentage of total Ag, varies considerably between different functional textiles. For instance, Benn and Westerhoff (2008) reported releases varying between <1% to almost 100% from six commercially available sock fabrics. Similarly, Geranio et al. (2009) and Lorenz et al. (2012) found that Ag released from Ag-functionalised textiles ranged from undetectable to about 45%. The variability in the results within each study is likely due to both the nature of the textile itself and the form of Ag present in the materials. In fact, Geranio et al. (2009) pointed out that mechanical stress is an important factor as about 10% of the textile weight can be lost during the lifetime of a product due to washing (Koehler et al., 2008) and it is reasonable to think that this loss may differ between textiles. Furthermore, it is also reasonable to assume that the speciation of Ag present in the textiles represents a critical parameter controlling Ag release. In the last decade the scientific literature and the number of patents covering methodologies for functionalizing textile materials using Ag, and Ag-NPs in particular, has increased dramatically (Radetic, 2013). For instance, Ag-NPs can be introduced by dipping the materials in suspensions of Ag-NPs, or they can be synthesized *in situ* by immersing the textiles in solutions of Ag salts and adding a reducing agent (Emam et al., 2013) and references therein). Another standard approach is to incorporate the Ag-NPs into the fibre matrix, therefore reducing release to a great extent (Geranio et al., 2009). These different methodologies most likely result in a number of different Ag species potentially being present in textiles. However, the literature investigating Ag speciation in textiles mainly focuses on laboratory materials and the information on commercial textiles is extremely scant. Impellitteri et al. (2009) used X-ray Absorption Near Edge Structure (XANES) spectroscopy to investigate the speciation of Ag in one antimicrobial sock textile before and after washing and found that Ag was present in a metallic form prior to washing but only accounted for 50% of the remaining Ag after washing with an hypochlorite/detergent solution due to partial conversion to AgCl. Based on results from washing studies, other authors have suggested that both ionic Ag and Ag₂S-NPs

may also be present in commercial textiles (Geranio et al., 2009; Lorenz et al., 2012).

Reliable information regarding Ag speciation and release during washing is essential knowledge required to decrease the uncertainties related to environmental exposure assessment of nanomaterials. Models that are being developed to predict environmental concentrations of NPs (Gottschalk et al., 2010, 2013) rely on information regarding input parameters as well as release rates, which are controlled by various factors including speciation. In this study, we aimed to significantly expand the knowledge base regarding Ag speciation in commercial textiles by undertaking XANES analysis of 5 commercial textile products. Clearly this knowledge is also relevant in the context of consumer information as manufacturers often provide limited information on their labels and these may not necessarily be correct. Furthermore, the release of Ag from textiles during two different washing procedures was investigated. Finally, the speciation of the washed textiles was also investigated as this provides information regarding the potential for further release from successive washings.

2. Materials and methods

2.1. Materials

Five commercially available and Ag-functionalized textile samples, which had previously been investigated for Ag release by Lorenz et al. (2012) were selected for this study (Table 1). While the Lorenz et al. (2012) study focused on the forms of Ag released during washing, this work focuses on the influence of different washing procedures on Ag release and on the speciation of Ag in the fabric pre- and post-washing. In order to facilitate comparison between these two studies, we have maintained the same sample numbering as that used by Lorenz et al. (2012). The total Ag concentration in the textiles ranged from 18 to 2925 mg kg⁻¹ and the materials were comprised of varying proportions of natural fibres, with the exception of two textiles which were completely synthetic. As noted in Table 1, the information provided on the product labels was often generic and Ag-NPs were only mentioned for product 6.

2.2. Washing procedure

Two textile washing procedures were utilised in this study. The first one, referred to here as LW (laboratory washing) was described in detail in Lorenz et al. (2012) and was based on the 'ISO 105- IS: 1994 (procedure A1S) for colour fastness to domestic and commercial laundering' (ISO, 1994) using the ECE-2 Colour fastness test detergent. In the second procedure, referred to as MW (machine washing), fabric pieces of 1.5–2.5 g were added to a regular washing cycle to simulate a washing event carried out in an average household by consumers. A 60 min program at 40 °C and 1200 rpm tumbling was applied (washing machine model: V-Zug AG, Unimatic F, type WA-UF) with Persil Megaperls

Table 1

Textile composition, Ag labelling information, total Ag and Ag released during the washing procedure. All data (except release during machine washing which was measured in this study) are taken from Lorenz et al. (2012).

Sample	Fibre composition	Product labelling regarding Ag	Total Ag (mg/kg)	Ag release from washing (%)	
				Lab washing	Machine washing
T1	41% polypropylene, 31% polyamide, 18% cotton, 10% wool	'Silver integrated' in polyamide	18 ± 2	0	5
T4	83% polyester, 17% wool	'Silver'	183 ± 10	20	22
T5	100% polyester	'Silver ions'	45 ± 8	14.8	n.a.
T6	80% cotton, 20% elastic yarn	'Nanosize silver particles are incorporated in cotton fibres'	2925 ± 10	23.5	60
T7	93% polyamide, 7% elastane	–	41 ± 0.4	17.6	80

as washing powder (see <http://mymsds.henkel.com/mymsds/DS.do?bu=UW&internet=true> for information on composition). Fabric pieces of all five investigated textile samples were washed once, together with 4.5 kg of medium soiled clothes. The washing experiment was repeated three times (each time including fabric samples of all five textiles). The samples were dried at room temperature and then digested with 3.5 mL of HNO₃ (65%) and 1 mL of H₂O₂ (30%) in a High Performance Microwave (MLS 1200 MEGA digestion system, EM-45/A Echaust Module). The Ag content was quantified by ICP-OES (ICP OES Perkin Elmer OPTIMA 3000).

In order to assess the transformation of species of Ag that are frequently found as a result of washing procedures (Lorenz et al., 2012), Ag-NPs, AgCl-NPs and a zeolite on which Ag was sorbed (as representative of ionic Ag) were subjected to washing procedures similar to those used for the textiles. The Ag-NPs were synthesised by reduction of 1 mM silver nitrate (AgNO₃) with 2 mM sodium borohydride (NaBH₄) in the presence of 200 mg L⁻¹ polyvinylpyrrolidone (PVP). PVP coated AgCl-NPs were prepared according to the method by Kim et al. (2010) in ethylene glycol and were resuspended in water after centrifugation. The NPs were characterised by dynamic light scattering (DLS; NICOMP 380 ZLS, Particle Sizing Systems, FL, USA) and scanning electron microscopy (SEM; Quanta 450 FEG ESEM, FEI Company, OR, USA). The Ag-NPs were polydisperse with the smallest size number-weighted mode at 6.2 ± 0.9 nm, while AgCl-NPs were bimodal with the smaller mode at 79.6 ± 12.3 nm (>92%, number weighted). SEM images of the NPs are reported in Fig. S1 (Supplementary Material). These materials were dispersed in 10 ml of washing liquid at 3.3 mg L⁻¹ (pre-heated to 40 °C), containing 4 g L⁻¹ of the washing powders described above. The concentration of 3.3 mg L⁻¹ was derived from an assumed loading of Ag in textiles at 50 mg kg⁻¹, which is within the range found and reported by Lorenz et al. (2012). The bottles were then placed on an end-over-end shaker for 30 min at 40 °C. Subsequently, 9 mL of the solution was frozen immediately and freeze-dried, which also pre-concentrated the Ag, for XAS analysis.

2.3. Silver speciation in textiles pre- and post-washing

Silver speciation was assessed by XANES. This technique was chosen as it provides the following advantages: it provides information regarding the overall Ag speciation; it is not limited to the analysis of the textile surface (in contrast to X-ray Photoelectron Spectroscopy, XPS); it does not depend on species crystallinity (in contrast to X-ray Diffraction, XRD); it is not limited to the detection of particles/NPs enriched in Ag (in contrast to electron microscopy). However, it should also be pointed out that definite attribution of Ag to a particular species is not always possible due to the similarity in spectral features of some of the Ag species of interest [especially Ag(I) bound to groups other than thiols].

XANES analysis was performed on all the textile samples pre- and post-washing and a number of Ag standards. The latter include: the pre- and post-washing samples of Ag-NPs, AgCl-NPs and Ag sorbed on zeolite described above; Ag carbonate (Ag₂CO₃), Ag nitrate (AgNO₃), Ag phosphate (Ag₃PO₄), Ag oxide (Ag₂O), Ag sulphate (Ag₂SO₄), Ag sulphide nanoparticles (Ag₂S-NPs synthesized by reaction of AgNO₃ with elemental sulfur in the presence of PVP) and Ag complexed by cysteine and histidine. These standards were diluted in cellulose to approximately 1000 mg Ag kg⁻¹ prior to analysis. The textile samples were folded several times and mounted, using polyimide tape, on a sample holder for analysis.

Silver K-edge XANES of the textiles were collected at the Materials Research Collaborative Access Team (MRCAT) beamline 10-ID, Sector 10 located at the Advanced Photon Source (APS), Argonne National Laboratory (ANL), Argonne, IL. (Segre et al., 2000). The electron storage ring was operating at 7 GeV in top-up mode. A liquid N₂ cooled double crystal Si(111) monochromator was used

to select incident photon energies and a platinum-coated mirror was used for harmonic rejection. The monochromator was calibrated by assigning the first derivative inflection point of the absorption K-edge of Ag metal at 25514 eV and a Ag metal foil spectrum was collected congruently with each sample scan. Powdered samples (not the textile samples) and standards were pressed into pellets and three XANES scans were collected for each sample in transmission and fluorescence mode using a 13 elements Ge detector. Pre- and post-washing samples of Ag-NPs, AgCl-NPs and Ag sorbed on zeolite were collected at the XAS beamline at the Australian synchrotron using a similar setup as described above and a 100 element Ge detector. The same standards were collected independently at the two beamlines. Principal component analysis (PCA) of the normalised sample spectra was used to estimate the likely number of species contained in the samples, whilst target transformation (TT) was used to identify relevant standards for linear combination fitting (LCF) of the sample spectra (ER, 1991). PCA and TT were performed using SixPack (Webb, 2005) while data normalisation and LCF were performed using Athena (Ravel and Newville, 2005). Fitting range was -30 to +100 eV relative to the Ag K-edge. For each sample, the combination of standards with the lowest residual parameter was chosen as the most likely set of components. It should be noted that any species included in the fitting solution representing values less than 10% of the total should be considered with caution as such low representation is at the very limit of the resolution capability of XANES (Manceau et al., 2002).

3. Results

3.1. Silver speciation in the unwashed textiles

The Ag K-edge spectra of the standards used in the LCF of the textile sample spectra are reported in Fig. S2. The spectrum of Ag-NPs is characterised by significant features with a white line position 15 eV above the absorption edge and two other prominent peaks approximately 36 and 71 eV above the absorption edge (corresponding to 25529, 25550 and 25585 eV in absolute energy). These are well in line with the peak positions reported for reference Ag foils (EXAFS Materials, Danville, USA). The spectrum of AgCl-NPs is also readily distinguishable by the presence of a sharp white line and a second, less intense peak about 16 eV above the white line. A sharp white line, but not the second marked peak, is also evident in the spectra of Ag nitrate, sulphate and Ag sorbed on zeolite. These spectra are in fact similar to each other and this should be considered when interpreting the LCF results. Similarly, the spectra of Ag₂S and Ag bound to cysteine are very similar and this should also be kept in mind when interpreting the LCF results.

By comparing the XANES spectra from the unwashed textiles (Figs. 1 and S3) with those from the standards reported in Fig. S2, it is immediately evident that Ag is present in the textiles as a mixture of different species/forms. Linear combination fitting indicates that Ag in particulate (metallic) forms dominates the speciation in T4, T5 and T7 (Table 2). In fact, the spectra for T4 and T5 both show the 3 main peaks identified previously for Ag-NPs. However, these spectral features are less marked than in the case of the Ag-NPs standards as a result of the presence of additional Ag species and in particular Ag₂S. In the case of T7, the presence of Ag-NPs is evidenced by the spectral feature which corresponds to the peak observed at 36 eV above the absorption edge (i.e. 2550 eV) for the Ag-NPs standard. Also, the peak observed in the AgCl-NPs standard at 16 eV above the white line (i.e. 25534 eV) is visible in T7. The presence of AgCl-NPs in T7 and of Ag-NPs in T4 was reported by the manufacturers and it is confirmed here, as is the presence of Ag₂S-NPs in T5 which was suggested by

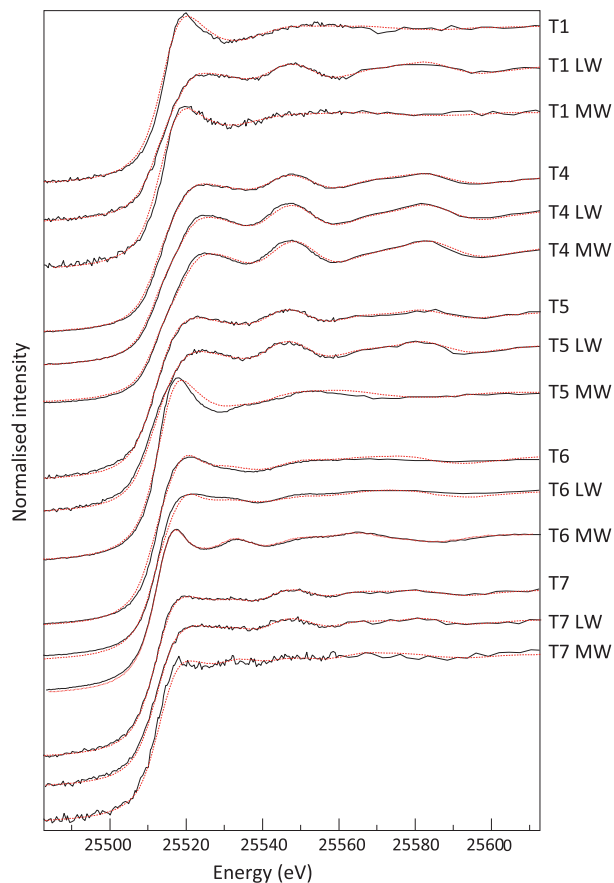


Fig. 1. Normalised Ag K-edge XANES spectra of unwashed and washed textiles. Dotted red lines show the best 4-component linear combination fit of reference spectra as documented in Table 2.

Lorenz et al. (2012). In contrast, the two other textiles show Ag XANES spectra that have a much stronger ionic Ag signature. In both cases the presence of a dominant white line peak and the absence of other characteristic features are similar to Ag salts and this is in line with the results from the LCF fitting (Table 2). The results from T6 are not in line with the manufacturer specification which indicates the presence of nanosize Ag particles in this product, but Ag phosphate is found to be dominant here.

Table 2

Best fit Ag speciation as identified by Linear Combination Fitting (LCF) of K-edge XANES. Species proportions are presented as percentages and the values in brackets show the percentage variation in the calculated values. Goodness of fit is indicated by the R-factor.

Textile	Ag-NPs	AgCl-NPs	Ag ₂ S-NPs	Ag oxide	Ag phos.	Ag nitr.	Ag sulf.	Ag-zeolite	R factor
<i>Unwashed</i>									
T1			16 (1.6)			52 (0.7)	14 (0.7)	18 (1.3)	0.0005
T4	55 (1.7)	11 (3)	32 (5)						0.0001
T5	43 (1.5)	17 (3)	35 (3)	5 (0.8)					0.0001
T6	12 (3)		16 (5)		67 (6)			5 (0.5)	
T7	36 (1.7)	36 (3)	14 (2)				14 (1.7)		0.0005
<i>Lab washed (LW)</i>									
T1	60 (2)		29 (6)		5 (4)			6 (3)	0.0002
T4	87 (2)		7 (4)	3 (3)					0.0002
T5	65 (2)	14 (5)	9 (3)	11 (3)					0.0003
T6	8 (3)		42 (4)		50 (3)				0.0004
T7	23 (2)	33 (4)	28 (3)	15 (2)					0.0002
<i>Machine washed (MW)</i>									
T1		25 (6)	35 (8)			10 (4)	19 (5)		0.0005
T4	92 (3)		4 (4)						0.0005
T5		32 (9)	24 (4)			27 (6)	15 (6)		0.0006
T6		59 (10)	20 (3)		14 (3)		7 (3)		0.0006
T7	7 (4)	42 (8)	38 (6)		9 (6)				0.0007

3.2. Effect of washing on silver speciation of pure compounds

The two washing procedures had significantly different effects on the Ag-NPs and the Ag-zeolite (Fig. 2 and Table 3). In contrast, AgCl-NPs were very stable during washing. The MW procedure caused an almost complete conversion of Ag to AgCl whereas LW caused a partial sulfidation of both Ag-NPs and Ag-zeolite, in line with the suggestion by Lorenz et al. (2012). Some of the Ag-zeolite also appeared to be converted to metallic Ag, as evidenced by the appearance of distinctive peaks at approximately 25550 eV and 25585 eV. Interestingly some trace evidence for Ag phosphate formation was found in the LW treatment but not in the MW treatment. The percentages of Ag phosphate reported are probably close to the resolution capability of XANES but are nevertheless reported as this finding is in line with the presence of phosphates in the LW detergent (while the MW detergent is P free). The formation of AgCl in the MW treatment cannot be explained on the sole basis of the Cl content in the washing solutions prepared using the two detergents, which is similar – 8.7 mg L⁻¹ in the phosphate-containing detergent (Lorenz et al., 2012) and 9 mg L⁻¹ in Persil used in the MW.

3.3. Effect of washing on silver speciation of textiles

The relative amounts of Ag released from the textiles during washing is given in Table 1. The data for LW are taken from Lorenz et al. while the MW results are from this study. For T1 and T4 the amounts released are very similar while for T6 and T7 the MW resulted in much higher release. In particular, T7, which only contained 41 mg kg⁻¹ of silver, released 80% through MW and this is reflected in the poor signal to noise in the XANES spectrum.

A first visual assessment of the XANES spectra reported in Fig. 1 indicates that while washing procedures caused considerable changes in Ag speciation in three textiles (T1, T5 and T6) the speciation in T4 and T7 remained fairly constant. Some general trends in changes in speciation caused by washing can be discerned. In the laboratory washed (LW) textiles T1, T4 and T5 the XANES spectra indicate a predominance of metallic Ag. This was present in considerable amount in the unwashed textile of T4 and T5 but not in T1 (Table 1). As the Ag release for T1 was negligible (Table 1), metallic Ag must have been formed in T1 as a consequence of the laboratory washing procedure. This is in line with the finding that spectral features for metallic Ag were found in the samples resulting from the washing of Ag-NPs and Ag-zeolite samples, which

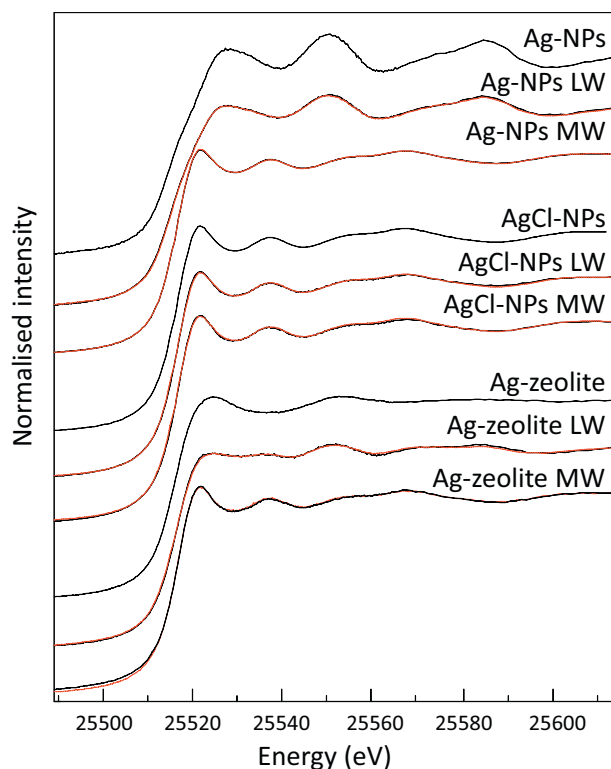


Fig. 2. Normalised Ag K-edge XANES spectra of unwashed and washed Ag-NPs, AgCl-NPs and Ag-sorbed zeolite. Dotted red lines show the best 4-component linear combination fit of reference spectra as documented in Table 3.

Table 3

Best fit Ag speciation in Ag-NPs, AgCl-NPs and Ag sorbed on zeolite washed in phosphate-containing detergent (used in the lab washing) and Persil (used in the machine washing) as identified by Linear Combination Fitting (LCF) of k-edge XANES. Species proportions are presented as percentages and the values in brackets show the percentage variation in the calculated values. Goodness of fit is indicated by the R-factor.

Ag form	Ag-NP	AgCl-NP	Ag ₂ S-NP	Ag phos.	R factor
<i>Lab washed (LW)</i>					
Ag-NPs	62 (5)		27 (1.5)	10 (1.2)	0.00003
AgCl-NPs		94 (1.4)	4 (0.8)	2 (1.1)	0.00005
Ag-zeolite	31 (0.7)	47 (2)	18 (1)	3 (1.3)	0.00006
<i>Machine washed (MW)</i>					
Ag-NPs		92 (1.8)	7 (0.9)		0.00005
AgCl-NPs		98 (0.6)	2 (0.6)		0.00004
Ag-zeolite		93 (1.5)	5 (0.9)		0.00009

suggests that metallic Ag can be retained or formed during LW (Table 2). In T4 and T5 the increase in metallic Ag representation could be due to either removal of Ag species different from Ag-NPs or to their conversion to Ag(0). Another effect of the washing procedure was the formation of Ag oxide in some textiles.

The machine washing (MW) procedure produced a different response, in terms of Ag speciation, in some of the textiles (Table 2 and Fig. 1). In particular, the Ag XANES spectra of T1, T5 and T6 for the two washings are significantly different. In all these cases, the AgCl spectral signature was much more evident in the machine washed textiles than in the laboratory washed materials (Fig. 1). This is reflected in the results of the LCF (Table 2) and is in line with the results obtained in the washing of Ag-NPs and Ag-zeolite samples that showed an almost complete conversion to AgCl as a consequence of the MW procedure with a commercial detergent. In fact, AgCl represented a much larger proportion of the total Ag

across the textiles after machine washing than in the unwashed materials or in the textiles washed under laboratory conditions. These changes in speciation seem to be the result of the transformation of metallic Ag, and Ag phosphate in T6, to AgCl (Table 2). A notable exception is represented by sample T4 (MW). In this case Ag-NPs dominated the spectra after both washing procedures, with significant reduction in the Ag₂S and AgCl content. Given that the Ag release from T4 is similar between LW and MW, it may be that these two are the major components of the released silver. Indeed, AgCl particles were previously found by Lorenz et al. (2012), although Ag₂S was only found in T5.

4. Discussion

The presence of multiple Ag species/forms in the textiles examined could be due to different causes. Comprehensive investigations of functionalised textiles in the scientific literature have shown that textiles can be functionalised with well-defined NPs under laboratory conditions (Zhang et al., 2012; Nguyen Khanh et al., 2013). However, it is reasonable to assume that upscaling of functionalization methodologies to the industrial level may result in different outcomes from those achievable under well-controlled laboratory conditions. It should also be noted that even in the case of scientific publications, Ag speciation in textiles is generally investigated using XRD and SEM, and less often with the aid of XPS. In fact, in a review on the determination of engineered nanoparticles on textiles, XANES is not even mentioned (Rezic, 2011). However, as argued above, XANES is possibly the most robust technique available in cases where the overall Ag speciation needs to be assessed. Another possible phase for transformations is during and after incorporation of Ag-NPs into or onto the textile. Some of the processes in the textile industry involve high temperature/extreme pH/high concentrations of other compounds and thus conditions are very different to those used in laboratory settings.

It is also possible that some of the species observed, particularly the Ag₂S, may be the result of processes occurring post-production. Tarnishing of Ag in air is a well-known phenomenon caused by the reaction of Ag with hydrogen sulfide present in air. As this is a surface process it is reasonable to expect that the rate of tarnishing may be accelerated in the case of Ag-NPs as they have a large surface-to-volume ratio. In fact, McMahan et al. (2005) showed that the rate of Ag-NPs tarnishing (as nanodisks of 60 nm diameter) was 7.5 times higher than that of bulk Ag under the same conditions. It is therefore not surprising that methods to reduce Ag-NPs tarnishing have been investigated (Chang et al., 2012). Considering the extremely low solubility of Ag₂S, this aspect needs to be further investigated in view of the potential consequences in terms of antimicrobial activity of the functionalized textiles and the release profile of Ag from these materials to the environment (e.g. through wastewater). These processes may occur anywhere during storage, shipment or in homes.

When considering the change in Ag speciation of the textiles caused by washing it should be kept in mind that these changes can be the result of two separate processes: (a) the conversion of some Ag species to others and (b) the preferential release of some Ag species from the textiles. Therefore, the interpretation of the XANES results needs to take into account the Ag release values reported in Table 1. These transformations find some explanation in the complex chemistry of Ag during washing. For instance, it seems that H₂O₂ which is often present during washing can lead to the formation of Ag oxides through Fenton-like reactions involving Ag ions (JA, 1962). At the same time, North and Bland (1920) reported the reaction of H₂O₂ with Ag₂O to form elemental Ag. In any case, it is apparent that in all laboratory washed textiles forms

of Ag that can be considered more soluble (nitrate, sulphate and Ag-zeolite) were drastically reduced. This is probably the result of combined Ag release during washing and conversion to more insoluble species. This cannot be simply explained on the basis of the initial Ag speciation in the textiles as the Ag XANES spectra for the unwashed T4 and T5 materials was similar but the effect of washing was much more marked for T5 (at least for machine washing) than for T4. These differences also cannot be explained on the basis of different preferential losses of some Ag species in these two textiles as the Ag release during washing was similar and, in both cases, limited.

The two washing procedures tested in this study resulted in different changes in Ag speciation which were textile dependent. In general however, the washing procedures seemed to promote the formation of more stable Ag species. As the changes in Ag speciation were in some cases substantial, it is unlikely that the preferential release of more soluble or less well attached Ag species/forms could be entirely responsible for the changes observed. Rather, chemical reactions are also likely to play a significant role. We cannot explain the different Ag-species formed in some textiles in lab-washing compared to home-washing. The chloride content of the detergent is similar (so we would expect to see similar amounts of AgCl formation). The main difference is that the lab-washing detergent is phosphate-containing while the home washing detergent is based on zeolites. Further controlled lab studies need to elucidate the role that different components of the washing liquid play in silver transformations.

The presence of more insoluble Ag species in laboratory washed textiles, in comparison to the original Ag speciation, could explain the results reported by Geranio et al. (2009); these authors washed nine Ag functionalised textiles two consecutive times (using the same washing procedure employed here) and observed a decrease in the Ag released during the second washing. These results are of interest in relation to the total release of Ag that can be expected as result of multiple washings. Furthermore, a change in Ag speciation as a consequence of washing is also likely to influence the antibacterial properties of the textiles over time. In fact, Lorenz et al. (2012) reported a reduction in the antimicrobial properties of T1 and T5 in their study but not in the other textiles tested here. However, these results indicate that bulk Ag speciation cannot be used to explain antimicrobial properties of textiles. This is not surprising as the antimicrobial properties are related to the release of Ag⁺, a species most likely representing a very small proportion of the total Ag in the textiles (and therefore below the XANES detection capabilities). The toxicity of Ag₂S for example is much lower than that of Ag(0) (Reinsch et al., 2012).

The observed differential reactivity of the Ag associated with the various textiles probably has different causes. It is likely that in addition to the differences in bulk speciation the size, surface functionality and/or passivation of the NPs surface also plays an important role. In addition, interactions between the textiles materials and the washing liquid could also provide an additional source of variability in the response of Ag to the washing procedures. For example, the two polyester based textiles (T4 and T5), whose initial Ag species are also comparable, behave similarly in LW (increase in metallic Ag, decrease in Ag₂S) but are considerably different in MW. It is clear that these variables are interconnected and reveal an additional layer of complexity in assessing Ag release.

As the outcome of washing procedures influence the performance of the textiles as well as the profile of Ag released during subsequent washing cycles (which is of environmental importance), these processes need further attention. For instance, the influence of particle properties could be investigated by functionalising different textiles with a number of well characterised Ag-NPs. Such a study would also elucidate the role that textile mate-

rials play in Ag transformation. However, this study clearly demonstrate the importance to investigate real-world systems as our work has shown that the speciation of Ag in commercial textiles is far from simple and, for some textiles, there are significant differences in the release and final Ag-speciation between lab-washed and home-washed textiles.

Acknowledgements

E.L. and E.D. are recipients of Australian Research Council Future Fellowships (FT100100337 and FT130101003). The funding support from the Australian Research Council is also acknowledged in relation to Discovery Project DP120101115. The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed a portion of the research described here. It has not been subject to Agency review and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred. MRCAT operations are supported by the Department of Energy and the MRCAT member institutions. Part of this research was undertaken using the XAS Beamline at the Australian Synchrotron, Victoria, Australia.

Appendix A. Supplementary material

Additional tables and figures containing information about the materials used and the XANES spectra of the standard compounds are available as supporting information. This material is available free of charge via the Internet at <http://www.sciencedirect.com>. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.03.116>.

References

- Arvidsson, R., Molander, S., Sanden, B.A., Hasselov, M., 2011. Challenges in exposure modeling of nanoparticles in aquatic environments. *Hum. Ecol. Risk Assess* 17, 245–262. <http://dx.doi.org/10.1080/10807039.2011.538639>.
- Benn, T.M., Westerhoff, P., 2008. Nanoparticle silver released into water from commercially available sock fabrics. *Environ. Sci. Technol.* 42, 4133–4139. <http://dx.doi.org/10.1021/es7032718>.
- Chang, M., Kim, T., Park, H.-W., Kang, M., Reichmanis, E., Yoon, H., 2012. Imparting chemical stability in nanoparticulate silver via a conjugated polymer casing approach. *ACS Appl. Mater. Interfaces* 4, 4357–4365. <http://dx.doi.org/10.1021/am3009967>.
- Emam, H.E., Manian, A.P., Siorca, B., Duelli, H., Redl, B., Pipal, A., Bechtold, T., 2013. Treatments to impart antimicrobial activity to clothing and household cellulosic-textiles - why "Nano"-silver? *J. Cleaner Prod.* 39, 17–23. <http://dx.doi.org/10.1016/j.jclepro.2012.08.038>.
- Er, M., 1991. *Factor Analysis in Chemistry*. John Wiley, New York.
- Geranio, L., Heuberger, M., Nowack, B., 2009. The Behavior of Silver Nanotextiles during Washing. *Environ. Sci. Technol.* 43, 8113–8118. <http://dx.doi.org/10.1021/es9018332>.
- Gottschalk, F., Sonderer, T., Scholz, R.W., Nowack, B., 2009. Modeled Environmental Concentrations of Engineered Nanomaterials (TiO₂, ZnO, Ag, CNT, Fullerenes) for Different Regions. *Environ. Sci. Technol.* 43, 9216–9222. <http://dx.doi.org/10.1021/es9015553>.
- Gottschalk, F., Sonderer, T., Scholz, R.W., Nowack, B., 2010. Possibilities and limitations of modeling environmental exposure to engineered nanomaterials by probabilistic material flow analysis. *Environ. Toxicol. Chem.* 29, 1036–1048. <http://dx.doi.org/10.1002/etc.135>.
- Gottschalk, F., Sun, T., Nowack, B., 2013. Environmental concentrations of engineered nanomaterials: review of modeling and analytical studies. *Environ. Pollut.* 181, 287–300. <http://dx.doi.org/10.1016/j.envpol.2013.06.003>.
- Impellitteri, C.A., Tolaymat, T.M., Scheckel, K.G., 2009. The speciation of silver nanoparticles in antimicrobial fabric before and after exposure to a hypochlorite/detergent solution. *J. Environ. Qual.* 38, 1528–1530. <http://dx.doi.org/10.2134/jeq2008.0390>.
- Ja, M., 1962. Higher oxidation states of silver. *Chem. Rev.* 62, 65–80.
- Kim, S., Chung, H., Kwon, J.H., Yoon, H.G., Kim, W., 2010. Facile synthesis of silver chloride nanocubes and their derivatives. *Bull. Korean Chem. Soc.* 31, 2918–2922. <http://dx.doi.org/10.5012/bkcs.2010.31.10.2918>.
- Koehler, A.R., Som, C., Helland, A., Gottschalk, F., 2008. Studying the potential release of carbon nanotubes throughout the application life cycle. *J. Cleaner Prod.* 16, 927–937. <http://dx.doi.org/10.1016/j.jclepro.2007.04.007>.

- Lorenz, C., Windler, L., von Goetz, N., Lehmann, R.P., Schuppler, M., Hungerbuehler, K., Heuberger, M., Nowack, B., 2012. Characterization of silver release from commercially available functional (nano)textiles. *Chemosphere* 89, 817–824. <http://dx.doi.org/10.1016/j.chemosphere.2012.04.063>.
- Manceau, A., Marcus, M.A., Tamura, N., 2002. Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. In: Fenter, P., Rivers, M., Sturchio, N.C., Sutton, S. (Eds.), *Reviews in Mineralogy and Geochemistry*, Applications of Synchrotron Radiation in Low-Temperature Geochemistry and Environmental Science, vol. 49. Mineralogical Society of America, Washington, DC, pp. 341–428.
- McMahon, M., Lopez, R., Meyer, H.M., Feldman, L.C., Haglund, R.F., 2005. Rapid tarnishing of silver nanoparticles in ambient laboratory air. *Appl. Phys. B-Lasers Opt.* 80, 915–921. <http://dx.doi.org/10.1007/s00340-005-1793-6>.
- Mueller, N.C., Nowack, B., 2008. Exposure modeling of engineered nanoparticles in the environment. *Environ. Sci. Technol.* 42, 4447–4453. <http://dx.doi.org/10.1021/es7029637>.
- Nguyen Khanh, V., Zille, A., Oliveira, F.R., Carneiro, N., Souto, A.P., 2013. Effect of Particle Size on Silver Nanoparticle Deposition onto Dielectric Barrier Discharge (DBD) Plasma Functionalized Polyamide Fabric. *Plasma Processes Polym.* 10, 285–296. <http://dx.doi.org/10.1002/ppap.201200089>.
- North, B., Bland, N., 1920. *Chemistry for Textile Students*, Cambridge, University Press, p. 135.
- Radetic, M., 2013. Functionalization of textile materials with silver nanoparticles. *J. Mater. Sci.* 48, 95–107. <http://dx.doi.org/10.1007/s10853-012-6677-7>.
- Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* 12, 537–541. <http://dx.doi.org/10.1107/s0909049505012719>.
- Reinsch, B.C., Levard, C., Li, Z., Ma, R., Wise, A., Gregory, K.B., Brown Jr., G.E., Lowry, G.V., 2012. Sulfidation of silver nanoparticles decreases *Escherichia coli* growth inhibition. *Environ. Sci. Technol.* 46, 6992–7000. <http://dx.doi.org/10.1021/es203732x>.
- Rezic, I., 2011. Determination of engineered nanoparticles on textiles and in textile wastewaters. *Trac-Trends Anal. Chem.* 30, 1159–1167. <http://dx.doi.org/10.1016/j.trac.2011.02.017>.
- Segre, C.U., Leyarovska, N.E., Chapman, L.D., Lavender, W.M., Plag, P.W., King, A.S., Kropf, A.J., Bunker, B.A., Kemner, K.M., Dutta, P., Duran, R.S., Kaduk, J., 2000. The MRCAT insertion device beamline at the Advanced Photon Source. In: Pianetta, P., Arthur, J., Brennan, S., (Eds.), *Synchrotron Radiation Instrumentation*, vol. 521, AIP Conference Proceedings, pp. 419–422.
- Vigneshwaran, N., Kathe, A.A., Varadarajan, P.V., Nachane, R.P., Balasubramanya, R.H., 2007. Functional finishing of cotton fabrics using silver nanoparticles. *J. Nanosci. Nanotechnol.* 7, 1893–1897. <http://dx.doi.org/10.1166/jnn.2007.737>.
- Webb, S.M., 2005. SIXpack: a graphical user interface for XAS analysis using IFEFFIT. *Phys. Scr.* T115, 1011–1014.
- Windler, L., Height, M., Nowack, B., 2013. Comparative evaluation of antimicrobials for textile applications. *Environ. Int.* 53, 62–73. <http://dx.doi.org/10.1016/j.envint.2012.12.010>.
- Wong, Y.W.H., Yuen, C.W.M., Leung, M.Y.S., Ku, S.K.A., Lam, H.L.I., 2006. Selectet applications of nanotechnology in textiles. *AUTEX Res. J.* 6, 1–8.
- Zhang, D., Toh, G.W., Lin, H., Chen, Y., 2012. In situ synthesis of silver nanoparticles on silk fabric with PNP for antibacterial finishing. *J. Mater. Sci.* 47, 5721–5728. <http://dx.doi.org/10.1007/s10853-012-6462-7>.

Silver speciation and release in commercial antimicrobial textiles as influenced by washing

Enzo Lombi^{a*}, Erica Donner^{a,b}, Kirk G. Scheckel^c, Ryo Sekine^a, Christiane Lorenz^{d,e}, Natalie Von Goetz^e and Bernd Nowack^d

^a Centre for Environmental Risk Assessment and Remediation, University of South Australia, Building X, Mawson Lakes Campus, South Australia 5095, Australia

^b CRC CARE, PO Box 486, Salisbury, South Australia 5106, Australia.

^c National Risk Management Research Laboratory, US Environmental Protection Agency, 5995 Centre Hill Avenue, Cincinnati, Ohio 45224, USA

^d Technology and Society Laboratory, Empa – Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, CH – 9014 St. Gallen, Switzerland

^e Institute of Chemical and Bioengineering, ETH Zurich, Vladimir-Prelog-Weg 10, 8093 Zurich, Switzerland

*Corresponding Author: enzo.lombi@unisa.edu.au Tel +61 8 8302 6267

Figure S1. SEM images of the AgCl-NPs (above) and Ag-NPs (below) used in the washing experiment.

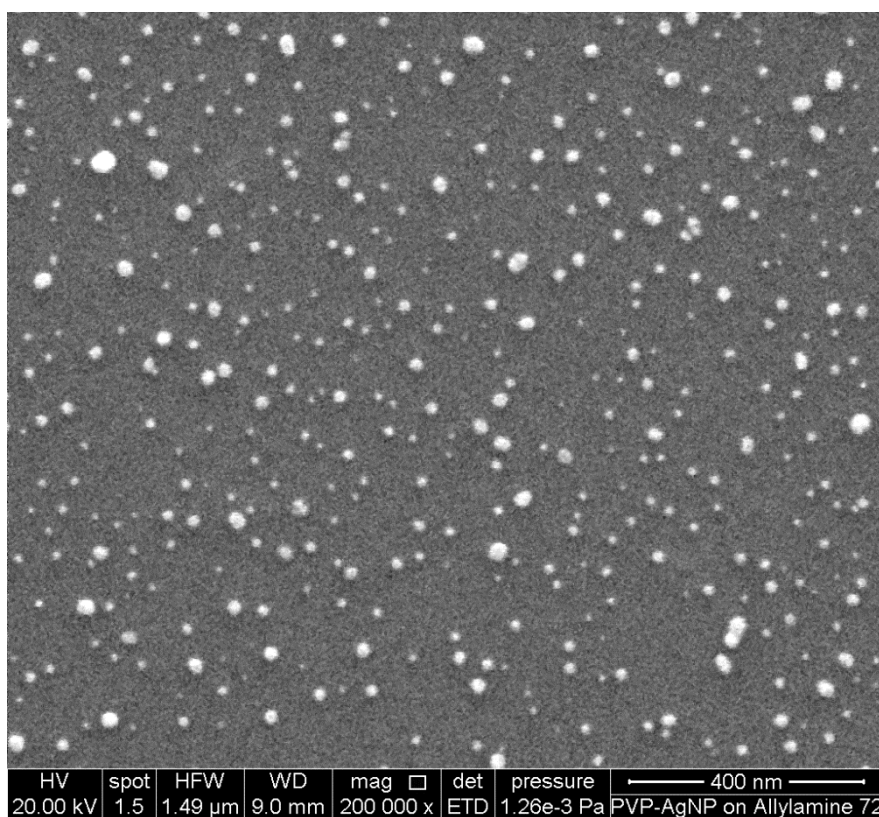
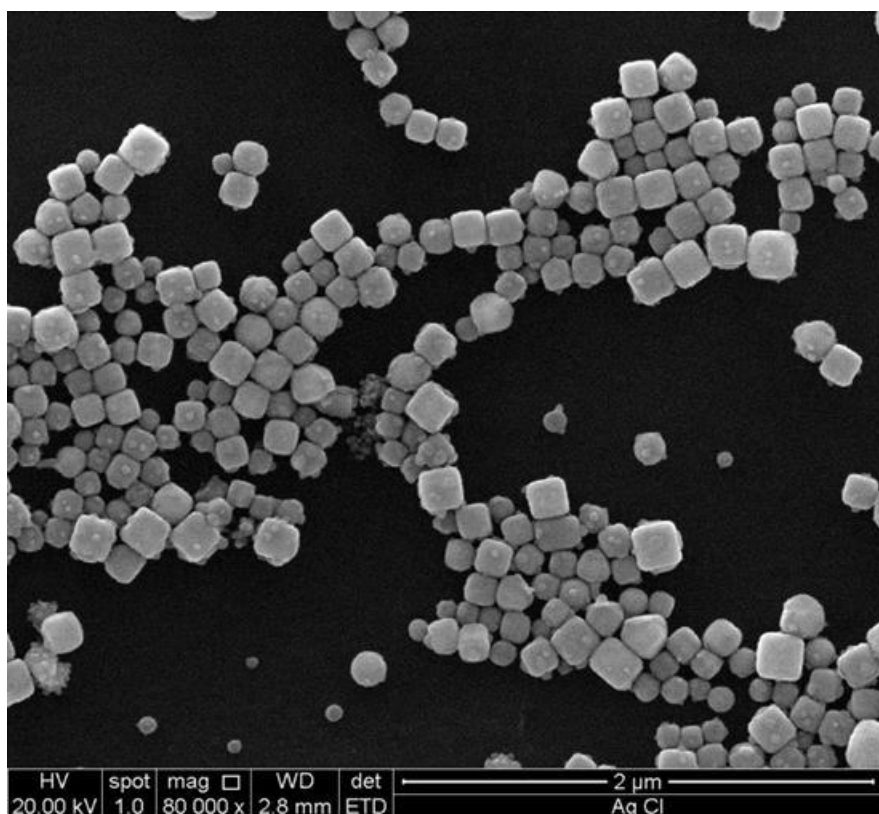


Figure S2. Normalised Ag K-edge XANES spectra of the standards used to fit the Ag textile spectra.

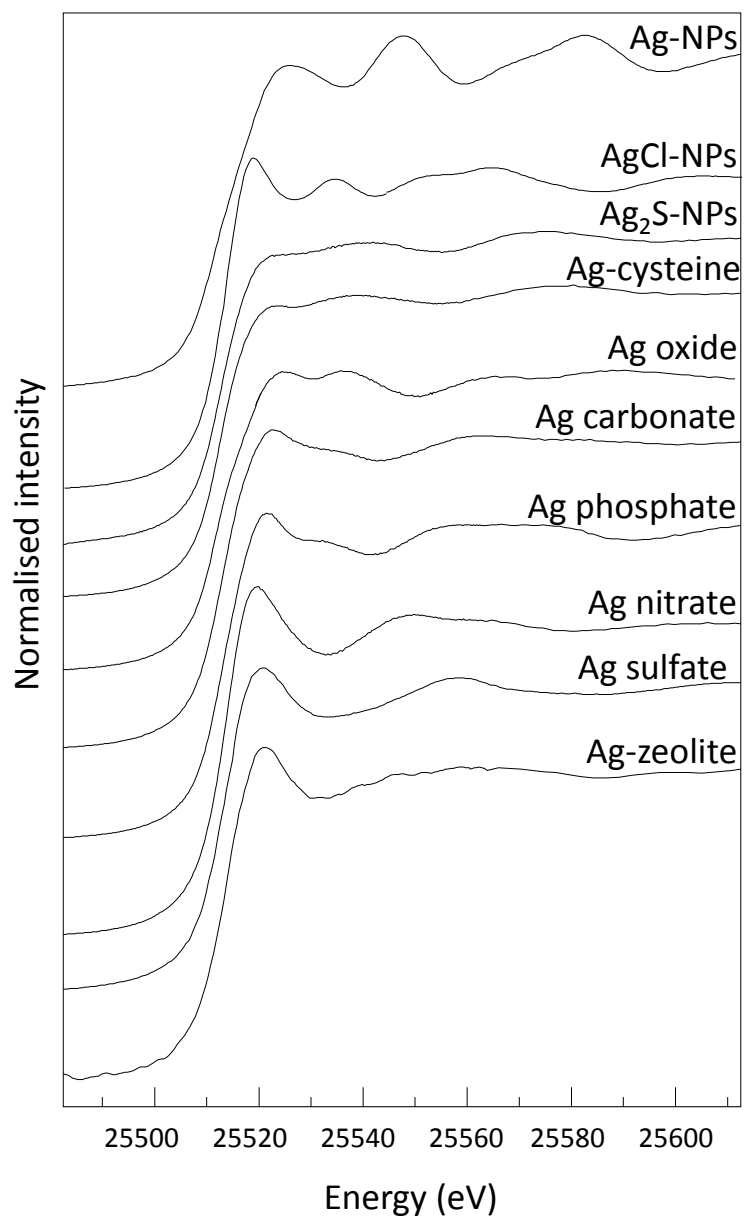


Figure S3. Normalised Ag K-edge XANES spectra of the unwashed textiles. Dotted red lines show the best 4-component linear combination fit of reference spectra as documented in Table 2.

