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

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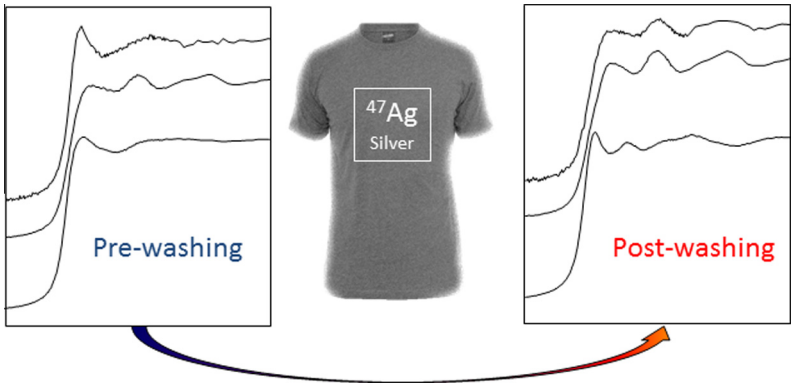
HIGHLIGHTS

- 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



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ABSTRACT

The use of nanoscale Ag in textiles is one 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, Ag_2S, 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.

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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 Ag_2S–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