Research Article   **Open Access**

Impact of Different Washing Conditions on the Release of Ag Species from Textiles

Joanna Kyzioł-Komosińska[1,2]*, Agnieszka Baran[3], Czesława Rosik-Dulewska[1,2], Justyna Czupiol[1], Sławomir Boncel[4] and Agnieszka Dzieniszewska[1]

[1]Institute of Environmental Engineering, Polish Academy of Sciences, 34 M. Skłodowskiej-Curie St., 41-819 Zabrze, Poland
[2]Department of Land Protection, University of Opole, 22 Oleska St., 45-052 Opole, Poland
[3]Faculty of Agriculture and Economics, University of Agriculture, 21 Mickiewicza Av., 31-120 Kraków, Poland
[4]Department of Organic Chemistry, Bioorganic Chemistry and Biotechnology, Silesian University of Technology, 4 Krzywoustego St., 44-100 Gliwice, Poland

Abstract

The paper investigates the Ag release from textiles (socks available in shops, cotton and viscose filled with Ag nanoparticles–AgNPs) into a washing solution under different conditions. The released Ag amount depended on various factors, such as test media (chemical composition, temperature and water volume), metal contents, and textile impregnation conditions. Furthermore, it turned out that the textile type and colour were the main parameters affecting the Ag release. The Ag concentration in the washing solution ranged between 0.015 µg/l and 4.44 µg/l (socks) and between 0.61 µg/l and 103 µg/l (AgNPs–filled cotton). The total Ag percentage released into water during one washing varied considerably among textiles (from less than 1 to 34%). In the tap water presence, the released Ag load decreased from 6.82 to 1.35 µg/l due to the AgCl and/or Ag_2CO_3 precipitation. The bleaching process had a strong effect on the quality and speciation of Ag rleased during the washing process. For example, the Ag concentration in the washing solution changed from 0.8 µg/l to 12.9 µg/l and was higher by 20 times (white socks) to 170 times (black socks) when compared with washing in water without any oxidising agent.

The washing of nano–Ag–treated textiles may have potentially released both ionic and particle forms as smaller AgNPs dissolved more rapidly than large AgNPs. The results of the present study demonstrate that the water solution containing Ag revealed a toxic effect on *D. magna* and *V. fischeri*. Among the tested species, *D. magna* was the most sensitive and revealed acute toxicity for low EC50 values. The *V. fischeri* response was less sensitive due to the physiological state of the bacteria.

Keywords: Nano–silver–filled textiles; Socks; Silver nanoparticles; Toxicity; Washing process

Abbreviations: AgNPs: Silver Nanoparticles; EC50: Half Maximal Effective Concentration; DI: Deionized Water; TOC: Total Organic Carbon; TU: Toxic Unit; *D. magna*: *Daphnia magna*; *V. fischeri*: *Vibrio fischeri*

Introduction

Due to the rapid nanotechnology progress and the expanding nanomaterial range (nanometals, nanometal oxides) having been produced and developed since the beginning of the 21st century, it is essential to take the potential nanomaterial impacts on humans and environment into consideration. A nanomaterial (material in nanoscale) is a material intentionally produced in the nanoscale so that it could have a specific property or composition [1]. Nanoparticles are clusters of atoms in the size range of 1–100 nm in at least one dimension. The metallic nanoparticles (Ag, Au, Cu and Zn) are the most promising agents. They demonstrate unique and considerably changed physical, chemical and biological properties when compared to their macroscale counterparts and dissolved salts. Such a situation is related to the fact that nanoparticles demonstrate high surface–to–volume ratio. Characteristic colour of noble metals in colloidal form (yellow for silver and red for gold) when compared with the colourless Ag ionic form has been used in the artistic glass dyeing since the 19th century, when the "nano" nomenclature was not known yet.

The nanoparticles are interesting for various applications (such as catalysts, optical sensing, antibacterial activity or data storage). Due to the nanometal properties, an increasing number of consumer and medical products is being used nowadays in Asia, North America and Europe. On the other hand, the nanoparticle properties pose problems to be faced by nanotechnology. The Ag nanoparticles (AgNPs) are one of the most widely used nanometals. They are present in over 250 consumer products, including domestic devices (fridges, vacuum cleaners, air conditioning), paints and varnish, textiles/textiles and clothes (sportswear, T–shirts and socks), plastics, cosmetics and detergents, or medical products (surgical gowns, dressing bandages, catheters, infusion systems, medical textiles) [2-4].

According to the Woodrow Wilson Database [5], creams and cosmetic items (32.4%), health supplements (4.1%), textiles and clothing (18.0%), air and water filters (12.3%), household items (16.4%) and detergents (8.2%) are the most important groups of products containing AgNPs. One of the AgNP applications is enhancing the antibacterial textile properties. Apart from consumer products containing AgNPs, the nanosized Ag colloidal solutions are available on sale. The solutions allow consumers to prepare antimicrobial textiles which may be used in kitchens, bathrooms, etc. AgNPs are used either to protect the products from the microbial growth effects or to protect the user from harmful microorganisms. AgNPs are effective against 650 disease–causing organisms in the body [6], even at low concentration levels ($<10^{-7}$ g/l), and relatively non–toxic for human cells. Due to the increased production of Ag–filled textiles, these materials are one of the major sources of the AgNP release into the environment. During washing, abrading, or discarding of the AgNPs–containing products,

Ag can easily release into wastewater and enrich the wastewater stream with Ag. Subsequently, Ag is transported into a wastewater treatment facility and ends up in surface water bodies which may be used as drinking water sources [7,8]. Ag may also deposit in the river sediments and soil, where it can stay for a long time or be absorbed by biological organisms. Therefore, Ag can act as eco–toxicological hazard; undergo biodegradation or bioaccumulate in the food chain [9]. Moreover, AgNPs may potentially disrupt helpful bacteria used in the wastewater treatment facilities or jeopardize aquatic organisms [10].

Ag can be introduced into the environment as nanoparticles, nanoparticle aggregates, or soluble ions [8]. Under oxidizing conditions, nano–Ag is found in fresh water in insoluble salts (bromides, chlorides and iodides). Under reducing conditions, Ag exists as a free metal. When the environment is rich in sulphur (organic thiol groups and inorganic sulphides), as during sedimentation processes in the wastewater treatment, the nanosize Ag sulphides are formed [11]. AgNPs and their derivatives may destroy and/or pass through the cell membrane and bind with the –SH groups in the cellular enzymes. Consequently, they decrease the enzymatic activity, which may change the metabolism of microorganisms, inhibit their growth and lead to the cell death [12,13]. The risk posed by AgNPs has not been clarified yet. Their widespread use could increase the Ag release in the environment, which may have a negative impact on ecosystems. The recent results of the acute toxicity tests support the theory that the AgNP effects on the aquatic organisms are mainly due to the Ag^+ release from nanoparticles [14]. Therefore, the Ag release from products into water or wastewater should be controlled. In North America in 2008, the AgNP concentration in surface water was at the level of nanogram per liter [15]. The AgNP concentration in wastewater was assessed to be 3 orders of magnitude higher. The background Ag concentrations in pristine waters were 0.01 mg/l [10]. The World Health Organization recommended the exposure limits for Ag compounds in drinking water at the level of 0.10 mg/l [16].

The American Conference of Governmental Industrial Hygienists established separate threshold limit values for the metallic Ag (0.1 mg/m^3) and soluble Ag compounds (0.01 mg/m^3). On the other hand, the permissible exposure limit (PEL) recommended by the Occupational Safety and Health Administration and the Mine Safety and Health Administration and the recommended exposure limit set by the National Institute for Occupational Safety and Health are established at the level of 0.01 mg/m^3 for all the Ag forms [17].

Many works on the Ag nanoparticles focus on the AgNP synthesis (including physical, chemical, and biological methods) and antibacterial activity of textiles [18-21]. There is still no information on the concentrations of Ag particles that may be released from textile products with Ag in their life cycle (especially when it comes to the release into the water environment during washing processes). The Ag release from different textiles and dependence between different washing conditions and Ag leaching have been discussed in a small number of studies [8,22,23]. Importantly, the type of chemical Ag species released during washing of textiles filled with AgNPs remains unclear [23-25]. Having the above–mentioned aspects in mind, the aim of this paper was to quantify the Ag release from commercially available socks containing AgNPs, and from cotton and viscose textiles filled with AgNPs under different conditions. The research was to take into account the washing medium kind (deionized and tap water), washing temperature (40°C, 60°C, 90°C), and presence of oxidizing agents. Additionally, the chemical species of the released Ag were detected in the washing solution. Due to the toxicity of the washing solutions containing Ag, toxicity tests were applied.

Material and Methods

Materials

The following materials were used in the experiment:

1. Socks with AgNPs available in the market (different colours and fibre composition); two pairs of socks had Ag mentioned on the label and three pairs of socks contained Ag in undeclared amounts;

2. AgNPs–filled cotton and viscose were prepared in a laboratory. The textiles were saturated with different Ag concentrations at different contact times of AgNPs–solution with textiles.

Sock textile characteristics

1. White colour – Hong Kong manufacturer; composition: cotton 70%, polyester 27%, lycra 3%, undeclared amounts of AgNPs;

2. Ecru colour – Polish manufacturer; composition: cotton 55%, lyocell with sea algae 23%, polyamide 19%, lycra (polyurethane) 3%, declared amount of AgNPs;

3. Grey colour – Polish manufacturer; composition: cotton 55%, lyocell with sea algae 23%, polyamide 19%, lycra (polyurethane) 3%, declared amount of AgNPs;

4. Graphite colour – Polish manufacturer; composition: cotton 55%, lyocell with sea algae 23%, polyamide 19%, lycra (polyurethane) 3%, declared amount of AgNPs;

5. Black colour – Hong Kong manufacturer; composition: cotton 70%, polyester 27%, lycra 3%, undeclared amounts of AgNPs.
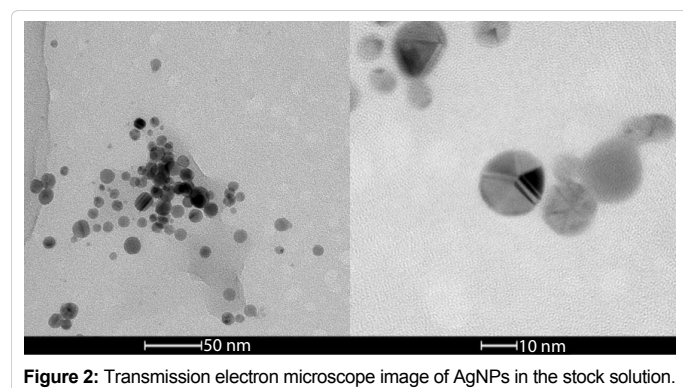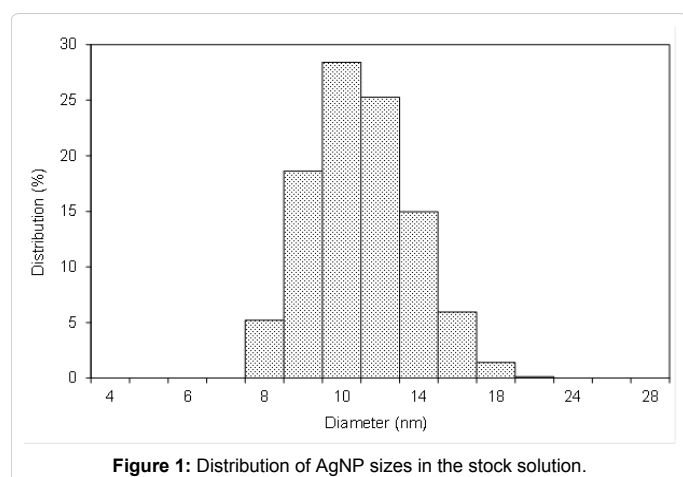
Laboratory Preparation of Textiles Containing AgNPs

The AgNPs–filled cotton and viscose preparation process was conducted at room temperature (25±2°C) and under normal pressure in a water solution without any extra reducing agents. The textiles were prepared according to following procedure: cotton and viscose textiles (10x15 cm; 5 g) were put into plastic boxes with 0.75 l of working solutions containing 4 different of AgNP concentrations (1, 5, 25 and 50 mg/l). The contact times were 15 and 60 min, respectively. Afterwards, the textile samples were separated from the solution and dried for 1 day at room temperature. The working AgNP solution was obtained with the serial dilution of the stock solution with deionized (DI) water. The stock solution was a commercial AgNP solution with the following properties: pH– 6.95; Eh– 106 mV; conductivity– 24 μS/cm; AgNP concentration– 140 mg/l; particle size– 8–18 nm (High Performance Particle Sizer model HPP5001, MALVERN Instruments (Figure 1). It contained the following reducing agents: acetic acid (83.02 mg/l) and propionic acid (32.18 mg/l). The organic acids with carboxylic (–COOH) groups provided the reducing conditions and stabilization of the AgNP forms. They also prevented the AgNP oxidisation to Ag^+. The presence of nano–Ag particles in the solution was confirmed with the transmission electron microscope analysis (TECNAI F20 TWIN, FEI Company; Figure 2). The particles were spherical and monodisperse.

Analytical Method

Measurement of total Ag content in textile samples

Socks, cotton and viscose textiles loaded with AgNPs were cut into squares (0.5x0.5 cm) with scissors. Afterwards, the samples underwent either wet or thermal mineralization. The wet mineralization (acid digestion) is based on the oxidizing action of strong acids, e.g. nitric acid (HNO_3). The digestion method (EPA SW846 Method 3050B) described by Benn and Westerhoff [8] was used for the textile degradation and Ag release into the solution.

Figure 1: Distribution of AgNP sizes in the stock solution.

Figure 2: Transmission electron microscope image of AgNPs in the stock solution.

On the other hand, the samples were ashed in quartz crucibles in a programmable muffle furnace at 550°C for 2 hours in the thermal digestion process. The remaining substance (powder) was put in 100 ml volumetric flasks, to which 4 ml of concentrated HNO_3 was added. The flasks were heated in a sand bath at 135°C. Subsequently, the solution was cooled and filled up with DI water. All the experiments were conducted in triplicate.

The Ag release from textiles

Socks, cotton and viscose textiles loaded with AgNPs were cut into squares (1×1 cm), placed in a glass bottle with water and washed in a water bath under different conditions for 1 hour, stirring every 10 minutes, without detergents. The textile samples were then separated from the solution and dried. After washing, the solution was stored in polypropylene vials in dark at room temperature. It was collected for the analysis. The total Ag concentration and pH were determined in the solutions. The released Ag concentration was determined in an unfiltered solution which was filtered through Whatman's cellulose nitrate membranes (0.1 μm).

Ag concentration determination

The Elan 6100 DRC–e ICP–MS spectrometer (Perkin Elmer) was used for quantitative analyses of the total Ag content in all the samples (socks and AgNPs–filled textiles) and Ag concentration released into the solution during washing process conducted under different conditions. The apparatus was equipped with a standard ICP quartz torch, cross–flow nebulizer and nickel cones. Samples and standards were delivered with a peristaltic pump. The spectrometer was optimized daily, to provide maximum intensity for ^{24}Mg, ^{115}In, ^{238}U and

minimum values for CeO/Ce (less than 3%) and Ba^{2+}/Ba (less than 3%), with a 10 μg/l solution (Mg, Cu, Rh, Cd, In, Ba, Ce, Pb, U) in 1% HNO_3 Elan 6100 Setup/Stab./Masscal Solution (Perkin Elmer). The ^{107}Ag concentrations were measured with the internal ^{103}Rh standard. The higher Ag contents in the solutions were determined with the flame atomic absorption spectrometry Avanta (PM) spectrometer (GBC) with a hollow Ag cathode lamp at λ=328.1 nm. The air–acetylene flame was used for atomization. The solutions obtained from the washing of AgNPs–filled cotton and viscose (initial AgNP concentrations: 25 and 50 mg/l) were used to determine the Ag^+ concentration with the potentiometric method. To do that, the CPI 505– Elmetron Poland ionometr (equipped with the EPS–1 glass–combined electrode and silver EAg/S–01 electrode) was used. The chloride half–cell was used for reference. The method detection limit was 0.01 mg/l. pH was measured with a pH–meter equipped with a glass-combined electrode.

The Ag content in each textile was normalized with respect to the textile dry weight and solution volume.

Different experiment conditions were taken into consideration for the Ag release:

1. Temperature effect: Ag was released from the textiles at 40, 60 and 90°C.

2. Water volume effect: the Ag content released from textiles was investigated (textile mass: water volume ratio of 1:100 and of 1:500; i.e. 0.5 g of textile+50 ml water and 0.5 g of textile+250 ml of water, respectively).

3. Water chemistry effect: Ag was released in the presence of deionized (DI) water and tap water. DI water (pH– 5.86; Eh– 181 mV; conductivity– 7.02 μS/cm) came from the Millipore Milli–Q water purification system and was used to prepare all the aqueous solutions. Tap water (pH– 7.27; Eh– 238 mV; conductivity– 941 μS/cm; alkalinity– 4.6 eq/l; Na^+ 7.6 mg/l; K^+ 1.6 mg/l; Ca^{2+} 89 mg/l; Mg^{2+} 27 mg/l; Cl^- 30 mg/l; SO_4^{2-} 64 mg/l; HCO_3^- 280.68 mg/l) was used for the Ag release under real conditions. The cation and anion concentrations were measured with the Metrohm ion chromatograph (Herisau Metrohm AG) equipped with the MetroSep A Supp 5 column (for anions) or Metrosep C2 column (for cations). The HCO_3^- amount was calculated on the basis of alkalinity and pH.

4. Bleaching agent presence effect in 1% concentration (5.0 ml for 500 ml of water bath; pH– 4.97; Eh– 360 mV). The bleaching agent level was similar as the level used under household conditions. The composition was: 5–15% of the oxygen–based bleaching agent, non-ionic and anionic surfactants and <5% Hexyl Cinnamal fragrance (as indicated in the characteristics). The oxygen–based bleaching agent contained sodium per carbonate ($2Na_2CO_3 3H_2O_2$). In water, sodium per carbonate breaks down into sodium carbonate and hydrogen peroxide:

$$2Na_2CO_3 \cdot 3H_2O_{2(aq)} \rightarrow 2Na_2CO_{3(aq)} + 3H_2O_{2(aq)} \tag{1}$$
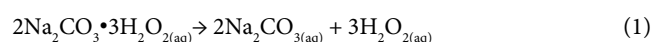
Hydrogen peroxide is the active oxidizing agent – it decomposes to oxygen gas:

$$2H_2O_2 \rightarrow H_2O + O_2 \tag{2}$$

In the solution (white sock washing in the presence of a bleaching agent), total organic carbon (TOC) values were determined with the TOC 5000A Analyser (Shimadzu). The TOC values were given after taking into account the blank control for the water + bleaching agent solution, which was 251.5 mgC/l.

5. Textile type effect: the Ag release from AgNPs–filled cotton and viscose was carried out at textile: DI water ratio (1:500) and at 20°C, 40°C, 60°C and 90°C

Antibacterial activity – Eco-toxicity test

The acute toxicity assessment of water solution containing Ag (obtained after washing) was performed with the following toxicity tests: Daphtoxkit F Magna and Microtox. Both tests are the most internationally used bioassays for the toxicity screening of chemicals and for toxicity monitoring of effluents and contaminated waters [26-30]. The crustacean acute toxicity was assessed through determining the inhibition of the *D. magna* mobility. The 24–h immobilization of *D. magna* bioassays was performed according to the Standard Operational Procedures of Daphtoxkit F Magna [31]. The Microtox test was used to assess the inhibition of luminescence in the *V. fischeri* bacteria [32]. The measurement analysis of the change in the luminescence was performed with the Microtox M500 Analyser. The standard test protocol was applied for water samples: 81.9% basic test (basic test, MicrotoxOmni software was used). The luminescence measurement was carried out before and after the 15-min incubation of the bacterial suspension with the studied sample. Three replicate samples were tested. The toxicity results were expressed as Effective Concentration (EC50 value), defined as the sample concentration that would produce a 50% reduction in the *V. fischeri* luminescence or 50% of the *D. magna* immobilization. The EC50 values were converted to Toxic Units (TU), according to the formula TU=1/EC50. The risk assessment system developed by Persoone et al. [33] was used to assess the water obtained after sock washing in terms of toxicity. Finally, the results were classified: class I: TU≤0.4 no significant toxic effect, no acute hazard; class II: 0.4<TU≤1 significantly toxic effect, low acute hazard; class III: 1<TU≤10 significantly toxic effect, acute hazard; class IV: 10<TU≤100 high acute hazard; class V: TU>100 very high acute hazard.

Results and Discussion

Total Ag content in sock samples

Regardless of the fact whether the Ag content was declared on the label or not, large Ag amounts were found in the investigated socks. The total Ag content in the studied socks (available in the Polish market) ranged from 8.232 to 20.94 mg/kg (Table 1). The Ag content in textiles was within the range observed by other authors. It was broad and changed between 1 and >1,000 mg/kg (Table 2). There were no statistically significant differences between the Ag content obtained during the wet and dry mineralization procedures (Table 1). Consequently, it was decided to take the Ag content obtained in the dry mineralization into account for further calculations.

Total Ag content in AgNPs–filled textiles

The total Ag content in the AgNPs–filled cotton and viscose mainly depended on: metal concentration in the solution used to prepare the antibacterial material, contact time for the textile and Ag solution, and textile type. Furthermore, the mineralization mode was an important parameter affecting the textile decomposition (Figure 3).

During the wet mineralization, the Ag content in the cotton samples changed from 3.99 to 148.11 mg/kg at 15–min contact time and for the viscose samples, the Ag content increased from 7.3 to 231.24 mg/kg (samples 1/15–50/15), whereas the initial concentration in the solution increased from 1 to 50 mg/l. The contact time prolongation by 4 times (to 60 min) for the solution with the AgNP textile resulted in the Ag content increase in textiles from 4.959 and 156.39 mg/kg and from 7.68 to 253.77 mg/kg (samples 1/60–50/60), respectively. Due to the

digestion with sample ashing in the oven and the remnant dissolution in the nitric acid solution (thermal decomposition), the total Ag content was higher in all the samples than after the wet mineralization. For the cotton samples, the value ranged between 4.748 and 161.66 mg/kg (15–min contact time) and between 5.756 and 182.08 mg/kg (60–min contact time). For the viscose samples, the values were 8.941–295.82 mg/kg and 8.847–304.96 mg/kg, respectively.

Viscose bound higher total Ag amounts than cotton in the entire initial Ag concentration range in the solution. Furthermore, the total Ag content increase observed for viscose during the dry mineralization was 15–28% in comparison with the wet mineralization. The value for cotton was 10–15%. The obtained results indicate stronger Ag binding with the surface functional groups in viscose (Figure 3).

During the textile preparation, the functional groups occurring on the cotton and viscose fibre surfaces bound the AgNPs efficiently, which facilitated the particle adsorption [34-36]. The SEM analysis (Figure 4) revealed small particles with different, non–homogenous distribution on the Ag–filled cotton and viscose fibres. The nanoparticles were clearly visible as white spots. For the AgNP concentrations of 1 mg/l and 50 mg/l on cotton and viscose, good distribution was discerned along the fibres (on their surface). The results indicated that Ag bound with fibres in the particle form. Cellulose is the main cotton and

Sock	White	Ecru	Grey	Graphite	Black
Wet mineralization	13.643 ± 0.320	20.938 ± 0.465	8.232 ± 0.136	16.810 ± 0.378	16.102 ± 0.411
Thermal digestion	13.825 ± 0.145	21.231 ± 0.265	8.540 ± 0.111	16.980 ± 0.210	16.380 ± 0.256

Table 1: Total Ag content (mg/kg) in socks after mineralization.

Textile types	Ag content	References
8 socks and one pair of trousers at varying proportions of natural fibres or only synthetic	1.5–2,925 and one without detectable Ag	[34]
Nine socks with different compositions	0.003–21.6	[22]
Textiles	0.9–1,358	[8]
Textiles	30–270	[23]
Textiles	0.99–15.1	[35]
Socks available in the Polish market	8.23–20.94	This paper
Cotton filled with nAg	4.959–182.08	This paper
Viscose filled with nAg	7.68–304.96	This paper

Table 2: Total Ag content in available textiles (mg/kg).
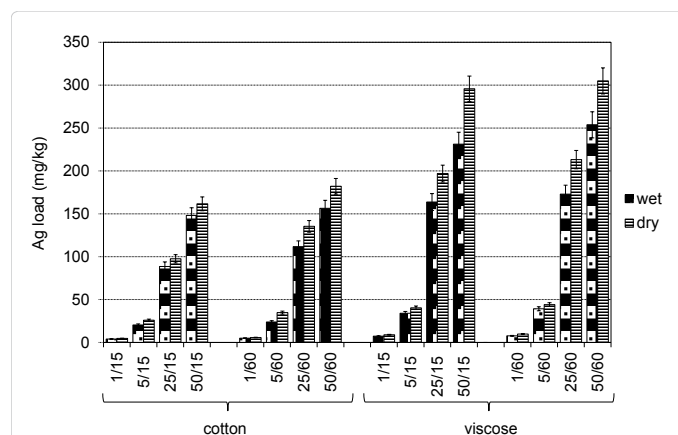
Figure 3: Ag contents in cotton and viscose samples with wet and dry mineralization (sample description – AgNPs initial concentration in solution (mg/l)/contact time (min).

viscose component. Cellulose makes 90–96% of cotton (based on the fibre weight) with β (1→4) linked D–glucose units $(C_6H_{10}O_5)_n$. It has an extensive surface area with functional hydroxyl (–OH) groups [37]. During the production of viscose (fibres of regenerated cellulose), a variety of plants (such as soy, bamboo or sugar cane) interacts with strong reagents, which reduces the polymerization degree and average number of glucose units in the cellulose polymer chain and increases the number of surface hydroxyl (–OH) groups and greater viscose reactivity (in comparison with cotton) [38] (Figure 5). The surface hydroxyl groups contribute to the increase in the number of the Ag particles bound by viscose.
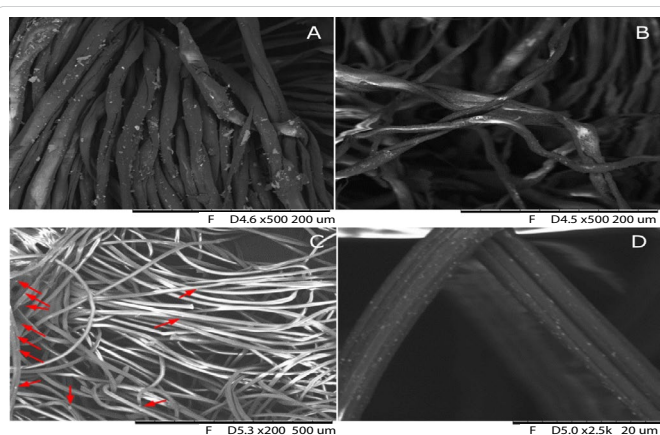
AgNP release from socks

Temperature and water volume effects: During the washing process, Ag was removed from the textile fibres into the solution. The released Ag amount depended on the volume of used water and its temperature. When the DI water was used and the applied textile mass: water volume ratio was 1:100, it was observed that the Ag release depended on the applied water temperature and sock type (particularly its colour). The laboratory research revealed that the Ag amount released from light colour socks (white and ecru) was higher than from the dark ones (grey, graphite, black). The highest Ag concentration in the solution in the washing was observed for water at 40°C for all the samples. It ranged from 4.441/4.295 µg/l (white/ecru socks) to 0.5255 µg/l (black socks). The released Ag loads were 0.4441/0.4295 mg/kg–0.05255 mg/kg, respectively. In comparison with the total Ag content in the socks, the Ag removal percentage changed from 3.26% (white socks) to 0.33% (black socks). The results indicate that the surface functional groups had a strong effect on the Ag release from textiles as the AgNPs are bound on the fibres due to the interaction with the surface functional groups. The surface functional groups originated from the cotton fibres. The surface functional groups may have also come from the dyes, which additionally increased their amount on the

colourful textile surfaces and also increased the textile ability to bind Ag and decrease its ability to release Ag. The application of higher washing temperature (60°C and 90°C) resulted in the decrease of the Ag released into the solution in the concentration range of 3.410–0.113 µg/l and 1.775–0.059 µg/l, respectively. The values corresponded to the Ag load of 0.311–0.0113 mg/kg and 0.1775–0.0059 mg/kg as well as to released Ag percentage vs. total Ag of 2.07–0.0702% and 1.3–0.0367% (Figure 6). When the volume of water for washing was increased 5 times (textile mass: water volume ratio of 1:500), the released Ag concentration was lower in the solution. At the same time, the released Ag load and Ag removal percentage from socks increased. The temperature and sock type influence was the same as for the lower water volume. The released Ag concentration in the solution was the highest for the white and ecru socks (at 40°C 3.96 and 3.30 µg/l, respectively). The released Ag load was 1.980 and 1.651 mg/kg, respectively. The Ag concentration after washing the grey, graphite and black socks was much lower. The values were 0.920, 0.853 and 0.432 µg/l, respectively. The released Ag load was 0.4600, 0.4268 and 0.2157 mg/kg, respectively (Figure 6). The released Ag percentage vs. total Ag in socks ranged from 14.52% (white socks) and 1.34% (black socks). When the samples were washed at 60 and 90°C, the Ag concentration in the solution was lower (2.54–0.063 µg/l and 0.550–0.015 µg/l, respectively). The released Ag load was 1.27–0.0313 mg/kg and 0.275–0.007 mg/kg, respectively. Regardless of the volume, all the washing liquids had pH of 6.08–7.05. In the washing solutions, the Ag^+ concentration in the samples was lower than the limit of quantification in the potentiometric method (0.01 mg/l). For that reason, the ionic Ag could not be determined in the solution.

Upto 98% of the released Ag was able to penetrate 0.1–µm filters. The results show that the particle size was less than 0.1 µm. Therefore, Ag occurred in the solution either as small nanoparticles or in the dissolved form as Ag^+. The study of Benn and Westerhoff [8] showed that during the washing of Ag–containing commercial socks in distilled water, up to 86% of Ag was released in the ionic form. The activity of nano–Ag vs. oxygen is well known. When AgNPs contacted with air and water, the Ag^+ ions formed during the washing of the AgNPs–filled textiles [39].

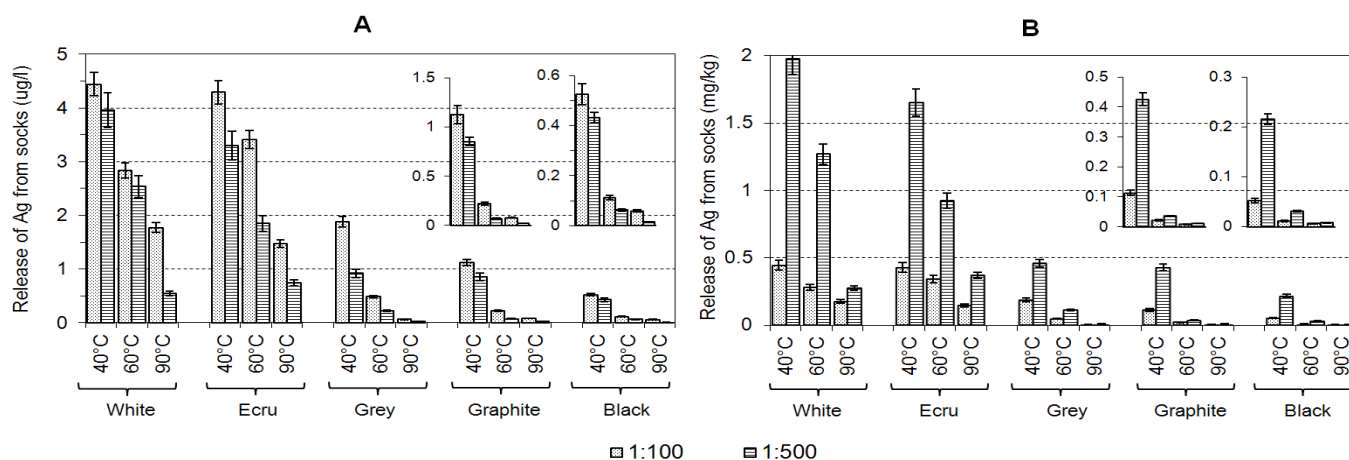### Water chemical composition effect

The effect of the water chemical composition on the Ag release from socks was investigated for DI and tap water in the batch system at 40°C at textile mass: water volume ratios of 1:100 and 1:500. The results showed that the chemical composition of water (together with the total Ag content and strength binding AgNPs on the fibre surfaces) had a significant role in the Ag release from textiles. When tap water was used for washing, both the concentration and loads of the released AgNPs decreased (Figure 7). The situation was observed for all the sock types. The Ag concentration in the tap water (textile mass: water mass=1:100) ranged from 1.54 µg/l (white socks) to 0.38 µg/l (black socks). In the DI water, the Ag concentrations ranged from 4.445 µg/l to 0.525 µg/l, respectively. When the textile mass: tap water volume ratio was 1:500, the released Ag concentration was between 0.58 µg/l and 0.32 µg/l. For the DI water, it increased from 3.96 µg/l to 0.432 µg/l, respectively. In the tap water presence and at sock mass: water volume ratio of 1:100, the released Ag loads decreased by 3.83–2.8 times (light colour socks) and by 1.79–1.38 (dark socks). When the discussed ratio was 1:500, the values changed by 6.82–4.29 (light colour socks) and by 2.24–1.35 times (dark socks). When Ag was released in the DI water presence, the pH value was approx. 6.69. In the tap water presence, pH was 8.15 to 7.67. The chemical analysis of tap water showed high conductivity (941 µS/cm) and the of Cl^- ion presence in water (30 mg/l). In the presence of the Cl^- ions, AgCl can be precipitated because the salt solubility is
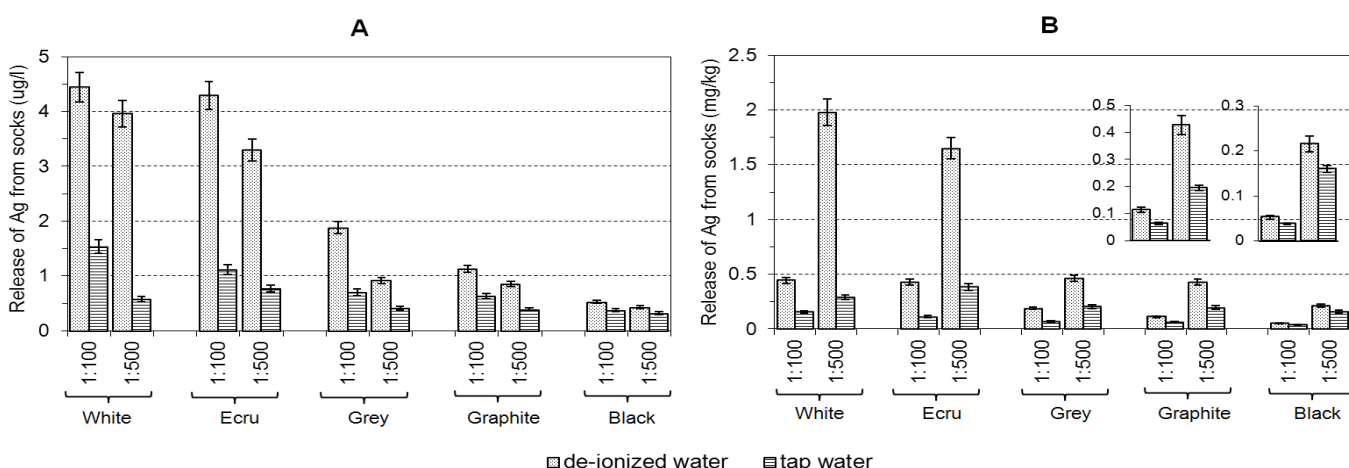

Figure 4: Cotton (A and B) and viscose (C and D) fibres after impregnation in a bath with 1 mg/l AgNPs (A and C) and 50 mg/l AgNPs (B and D).
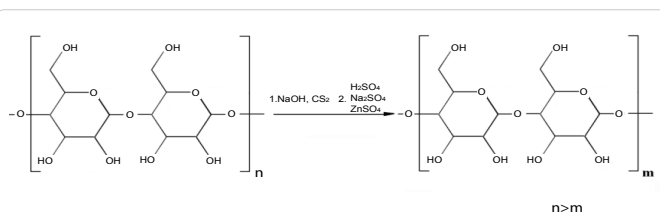
Figure 5: Diagram of the cellulose transformation process.

Figure 6: Release of Ag from socks in µg/l (A) and mg/kg (B) at sock mass: water volume ratio of 1:100 and 1:500.

Figure 7: Effect of water chemical composition on the Ag release from socks (µg/l (A) and mg/kg (B)).

very low and the solubility constant K_{sp} for AgCl is equal to 1.77×10^{-10} mol^2/l^2 at 25°C. Thus, the solubility is 1.33×10^{-5} mol/l. An additional source of the common ion chloride present in the solution may lead to the AgCl solubility decrease (common–ion effect). The high pH of the washing solutions (8.15 to 7.67) and high concentration of ligands in tap water can cause the Ag complexation and precipitation [40]. The results of the study conducted by Impellitteri et al. [25] suggested that during the washing metallic Ag is oxidized and transformed into AgCl. The discussed laboratory experiment consisted in the chloride acid solution addition to the AgNP solution and to the Ag$^+$ solution with the same concentrations and volumes. The experiment showed that a lower volume of the acid solution was needed for the AgCl precipitation from the Ag$^+$ solution than from the AgNP solution.

The Ag sensitivity strongly depends on the Cl$^-$ ion concentration. Moderate Cl$^-$ levels interact with Ag (nanoparticle and ionic forms) and precipitate as AgCl. Consequently, the available Ag level decreases. However, higher amount of Cl$^-$ results in the repeated Ag dissolution [41]. The tap water contains sulphate ions (64 mg/l). Due to the Ag$_2$SO$_4$ solubility (0.015326 mol/dm^3), this phase is unlikely to have formed. Mitrano et al. [40] proposed a mechanism consisting in the sulphur reduction and subsequent formation of the Ag–S particles. The presented washing experiment was conducted under oxidation

conditions (pH 7.67–8.15 and Eh 220–230 mV). The S species analysis based on the in Eh–pH diagrams [42] indicated the unlikeliness of the sulphide phase formation under such conditions. The study of Lombi et al. [43] demonstrated that the Ag species in the commercial textiles varied between different textiles (Ag(O), AgCl, AgS, Ag–phosphate and ionic Ag). They also demonstrated various release abilities. The chemical analysis of tap water demonstrated the presence of HCO$_3^{2-}$ anion and Ca^{2+} and Mg^{2+} cations (280.68 mg/l, 89 mg/l and 27 mg/l, respectively). At high temperature, CaCO$_3$ is precipitated (according to the reaction: Ca^{2+} + 2HCO$_3^-$ + H$_2$O + CO$_2$), which contributes to the precipitation/co–precipitation of Ag$_2$CO$_3$ due to the very low its solubility constant (K_{sp}=8.46×10^{-12} mol^2/l^2). The Ag concentration decrease in the tap water during washing was a complex process, which depended on the chemical composition of water.

Bleaching agent presence effect

The bleaching agent impact (concentration of 1%; 5 ml in 500 ml of water) on the Ag release was investigated for all the socks at textile mass: DI water ratio of 1:500 (Figure 8). For all the studied textiles, a significant release of Ag in the solution was observed after the bleaching agent was added because hydrogen peroxide decomposes into water and oxygen (equation 2). The oxidising effect depended on

the washing process temperature and sock colour. It was found out that the released Ag contents increased when the temperature rose. The maximum Ag concentration (12.9 µg/l) was found in the ecru sock washing solution at 90°C. At 40°C, the released Ag concentration and loads in the solution in the oxidising agent presence were higher by 1.24–1.88 times for all the socks than in the situation when the oxidising agent was absent. At 90°C, the released Ag content was 23.29 and 17.38 times higher for the white and ecru socks and 100–171 times higher for the colourful socks (Figure 8). At the same time, the TOC content in the white sock washing solution in the presence of a bleaching agent at 40, 60 and 90°C was 230 mgC/l, 313.6 mgC/l and 356 mgC/l, respectively. When the bleaching agent was not used, the TOC contents in the washing solution were 5.67–6.79 mgC/l. The results demonstrate that the oxidising properties of the bleaching agent improved with the increasing temperature. Oxygen released from H_2O_2 (equation 2) and may have also oxidised the cotton fibres in the socks and dyes incorporated in the fibres. Consequently, the Ag bound to the cotton fibres and dyes may have also been oxidised. Consequently, the Ag was higher released from colourful textiles. The enhancement in the hydrogen peroxide decomposition at high temperature was due to the favourable temperature effect in the increasing kinetic energy of the bleaching species and in the increasing swelling of cotton fibres. This resulted in higher accessibility. Therefore, the oxidizing species could easily penetrate the bulk of the fibre and remove the non–cellulose matter and dyes [44]. The AgNP oxidation with H_2O_2 was thermodynamically feasible with the standard redox potential.

Despite the total Ag concentration increase in the solution, in the oxidising agent presence, the Ag^+ ion concentration in the solution was undetectable with the potentiometric method. In order to define the influence of the oxidising agent presence on the Ag species in the solution, an experiment was conducted. It consisted in determining the total Ag and Ag^+ concentrations in the solutions with AgNPs (concentrations of 1, 10 and 50 mg/l) without or in the presence of the oxidising agent (concentration of 1%) (Table 3). The solutions were kept at 40, 60 and 90°C in the water bath for 1 hour. Afterwards, the Ag_t and Ag^+ concentrations were determined with AAS and potentiometric methods, respectively. The results are shown in Table 4. They indicate that the Ag^+ ion concentration increased with the solution temperature and oxidant concentration. In the presence of the bleaching agent and at 60 and 90°C, precipitation of a grey–black solid phase and decrease in

the total Ag concentration in the solution with 50 mg/l were observed for the AgNP concentration of 50 mg/l. The precipitate was soluble in both the ammonia solution and concentrated nitric acid. It yielded a brownish solution containing the Ag^+ ions, which indicated that the precipitate was Ag_2O.

Glover et al. [45] observed that in the vicinity of the parent Ag particles, smaller Ag nanoparticles are formed via the oxidation to Ag^+ ions and the subsequent reduction to the daughter Ag nanoparticle forms. The studies of Benn et al. [23], Farkas et al. [24] and Impellitteri et al. [25] showed that during washing of textiles filled with AgNPs, Ag is released. However, the chemical species of the released Ag remains unclear in most studies.

Temperature (°C)	Ag^+	Ag_t	%Ag^+	Ag^+	Ag_t	%Ag^+
	1 mg/l AgNPs			1 mg/l AgNPs + 1 % oxidant		
40°C	0.08	0.99	8.08	0.98	1.05	93.33
60°C	0.47	0.99	47.48	1.05	1.05	100
90°C	0.65	0.98	66.33	1.05	1.05	100
	10 mg/l AgNPs			10 mg/l AgNPs + 1 % oxidant		
40°C	0.85	10.1	8.41	9.6	10.0	96.00
60°C	2.03	10.0	20.3	9.8	10.0	98.00
90°C	3.15	10.0	31.5	9.9	10.0	99.00
	50 mg/l AgNPs			50 mg/l AgNPs + 1 % oxidant		
40°C	1.96	49.5	3.96	32.7	49.5	66.06
60°C	2.86	49.5	5.78	35.4	35.5	99.70
90°C	3.66	49.5	7.40	32.0	32.0	100

Table 3: Ag^+ and Ag_t concentrations in the AgNP solution after heating (mg/l).

Cotton samples C_o/time/T	Ag_t (µg/l)	Ag^+ (µg/l)	% of ionic form	Cotton samples C_o/time/T	Ag_t (µg/l)	Ag^+ (µg/l)	% of ionic form
25/15/25°C	27.74	11.5	41.45	25/60/25°C	39.42	22.1	56.06
25/15/40°C	38.58	21.4	55.47	25/60/40°C	48.00	28.5	59.37
25/15/60°C	67.03	41.8	62.36	25/60/60°C	70.01	30.5	78.18
25/15/90°C	57.97	52.3	90.22	25/60/90°C	64.95	59.2	91.15
50/15/25°C	59.25	23.3	39.32	50/60/25°C	65.39	33.1	50.62
50/15/40°C	74.52	40.1	53.81	50/60/40°C	81.29	45.3	55.73
50/15/60°C	99.11	59.4	59.93	50/60/60°C	103.0	64.3	62.42
50/15/90°C	68.99	61.9	89.72	50/60/90°C	81.85	71.8	87.72

Table 4: Ag species in the solution after the washing process of cotton filled with AgNPs.

Figure 8: Bleaching agent effect on the Ag release from socks (µg/l (A) and mg/kg (B)).
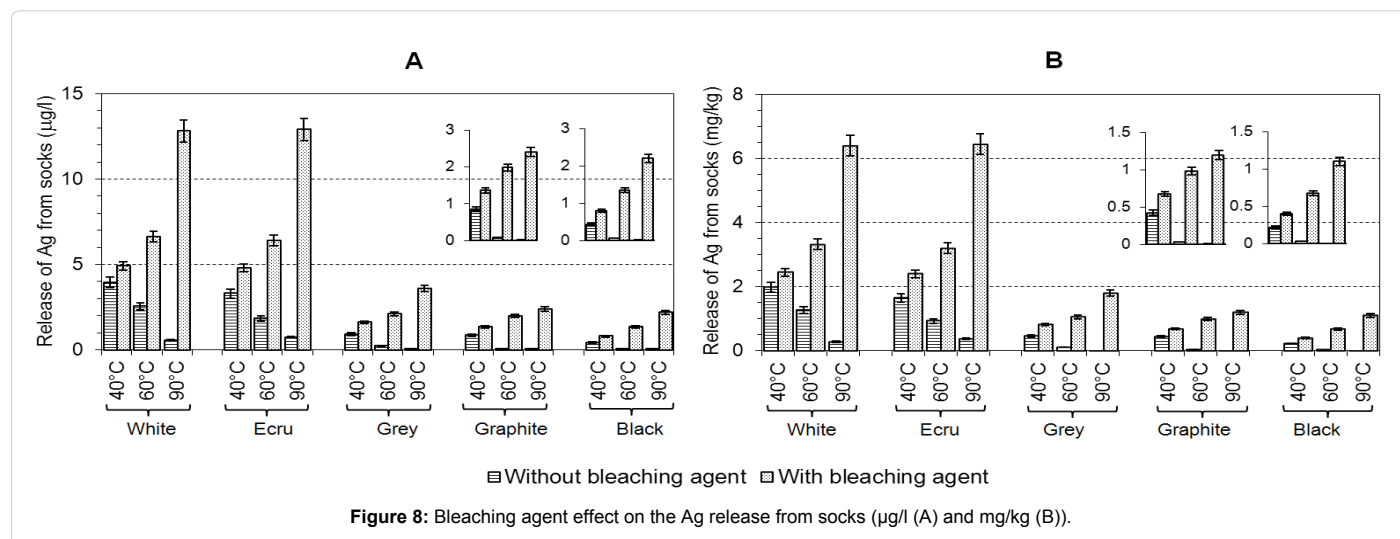
Ag release from cotton and viscose - effect of textile type

The Ag release from textiles filled with AgNPs during the washing process with DI water depended strongly on the textile structure. The released Ag concentration and load from cotton filled with AgNPs was higher than from viscose prepared under the same conditions. The amount of Ag removed from the cotton fibres to the solution depended on the washing temperature and total Ag content in the washed textiles. At the low AgNPs content (initial Ag concentration in the impregnation solution: 1 mg/l) in cotton, the released Ag concentration and load increased with temperature from 0.61 to 1.21 µg/l and 0.312 mg/kg to 0.6051 mg/kg, respectively (contact time=15 min) and from 0.64 to 9.499 µg/l and 0.3199 mg/kg to 1.324 mg/kg (contact time=60 min). The highest Ag amount was released at 90°C (Figures 9A and 9B). When higher Ag concentrations were used for impregnating cotton, the highest Ag concentration and load were released at 60°C. The effect of the initial filling AgNP concentration (C_o) of on the Ag amount released into the solution was as follows:

1. For C_o 5 mg/l: Ag was released into the solution in the range of 5.37–8.06 µg/l (2.683 mg/kg–4.028 mg/kg) for contact time of 15 min, and 8.29–17.47 µg/l (4.146–8.734 mg/kg) for contact time of 60 min;

2. For C_o 25 mg/l: Ag was released into the solution in the range of 27.74–67.03 µg/l (13.858–33.48 mg/kg) for contact time of 15 min, and 39.42–70.01 µg/l (19.71 to 35.03 mg/kg) for contact time of 60 min;

3. For C_o 50 mg/l: Ag was released into the solution in the range of 59.25–99.11 µg/l (29.60–49.54 mg/kg) for contact time of 15 min, and 65.39–103.01 µg/l (32.72–51.52 mg/kg) for contact time of 60 min.

The Ag percentage removal from cotton ranged from 6.57 to 33.77% at 15–min contact time and from 6.56 to 32.94% at 60–min contact time. The pH values were 6.08–7.60 and the pH increase with temperature was observed.

The Ag removal from viscose filled with AgNPs was considerably lower. Moreover, the highest released Ag loads were observed at 90°C regardless of the initial Ag concentration in the solutions used for the textile impregnation (saturation). The effect of the initial concentration on the Ag release into the solution was lower than for cotton. The Ag concentration in the solution after washing was 0.060–16.51 µg/l for textiles impregnated for 15 min and 0.120–20.95 µg/l for textiles impregnated for 60 min. The released Ag load was 0.0322–8.246 mg/kg and 0.0599–10.459 mg/kg, respectively. The Ag percentage removal ranged from 0.36 to 3.566% and from 0.6087 to 4.12%, respectively. The washing process for viscose occurred at lower pH than for cotton. It ranged from 4.41 to 6.11. Similarly to cotton, the pH increase with temperature was observed.

The results indicate that the textile structure (particularly the content of surface functional groups) affected the amount of Ag impregnating the textile and Ag binding strength on the fibre surfaces. It also played an important role in the Ag release into water. After the washing of AgNPs-filled cotton (C_o: 25 mg/l and 50 mg/l) at different temperatures, the Ag^+ ion concentration in the solution was determined with the potentiometric method with ion-selective electrodes (ISEs). The value was compared with the total released Ag amount determined with AAS. The result indicated that the Ag^+ ion concentration in the solution was dependent on the temperature. Its lowest value was observed at 25°C and increased with the rising temperature (Table 4).

The percentage of Ag^+ released from the cotton samples changed from 42.87–56.90% at 25°C to 15.57–18.69% at 90°C.

When the elemental Ag nanoparticles are in contact with water and dissolved oxygen coming from air, the Ag ions are released from the surface of textile filled with AgNPs in accordance with the equation:

$$O_{2(aq)} + 4H^+ + 4Ag \rightarrow 4Ag^+_{(aq)} + 2H_2O \qquad (3)$$
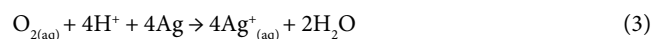
The effects of O_2 can be explained with the fact that the electron transfer from the Ag particles to the solute occurred [39,46].

Liu and Hurt [39] reveal that for a water solution under air-saturated conditions, the nano–Ag particle oxidation is observed in the entire range of the investigated nanoparticle concentration, whereas the Ag ion release from the nanoparticle surfaces increases with the rising temperature. The results obtained in this experiment show a similar distribution of Ag^+ ion in the function of temperature.

For textiles containing metallic Ag, the Ag(O) oxidation to Ag(I) in contact with water is a prerequisite for the appearance of the Ag^+ ions in the solution [22].

The AgNP oxidation process with dissolvent oxygen depended on the AgNPs size. The smaller the nanoparticles are, the larger the surface available for the interaction is, which results in a higher specific activity. Compared to larger AgNPs, small AgNPs release more Ag^+ ions [41,47]. Smaller AgNPs (5 nm) dissolved more rapidly than larger AgNPs (50 nm) in aqueous systems, which could be due to larger fraction of the surface atoms (higher specific surface area) in smaller AgNPs or due to lower redox potentials of smaller AgNPs [48]. The size of AgNPs used in the discussed experiments ranged from 8 nm to 18 nm, which suggests that AgNPs could be easily oxidised and dissolved easily (Table 4).

The research carried out by Silva et al. [49] showed that the pseudo–first–order equation fitted well with the data on the Ag^+ ion release from the plant cellulose fibres (µm) filled with AgNPs. This suggests that the Ag oxidation is a stage limiting the Ag release process.

Eco-toxicity test

The toxicity of a water solution containing Ag is presented in Table 1. *D. magna* showed higher sensitivity to Ag than *V. fischeri*. The EC50 values for *D. magna* were 46 times lower than for *V. fischeri*. The lowest EC50 value was determined for samples C (Cotton 50/60/60°C). The highest EC50 value was determined for samples A (*D. magna*) and B (*V. fischeri*) (Table 5). According to the TU values obtained for *D. magna*, all the studied samples should be classified as class IV toxic compounds (high acute hazard) and for *V. fischeri* as class III toxic compounds (acute hazard). Different research studies [28,30] showed that the lowest EC50 value <1 mg/l classifies chemicals as very toxic to aquatic organisms; 1–10 mg/l=toxic to aquatic organisms; 10–100 mg/l=harmful to aquatic organisms; >100 mg/l=not classified. In the research carried out for this study, the water extracts with Ag were very toxic (*D. magna*) and toxic (*V. fischeri*) for aquatic organisms. The release of the discussed nanoparticles from household products into wastewater streams and further into the environment may pose a threat to the 'non–target' organisms, such as microbes and aquatic organism [50]. It is also well known that AgNPs are most toxic to the aquatic organisms [51,52]. Different authors discovered several mechanisms to explain the toxic effect of Ag nanoparticles: 1) the presence of the AgNPs themselves; 2) the release of Ag^+ from nanoparticles; 3) free radicals generated during dissolution in the AgNP suspension [53,54] reported that the toxicity of AgNPs was caused by the Ag ions emitted from the nano–material surface. Consequently, the toxicity mechanisms
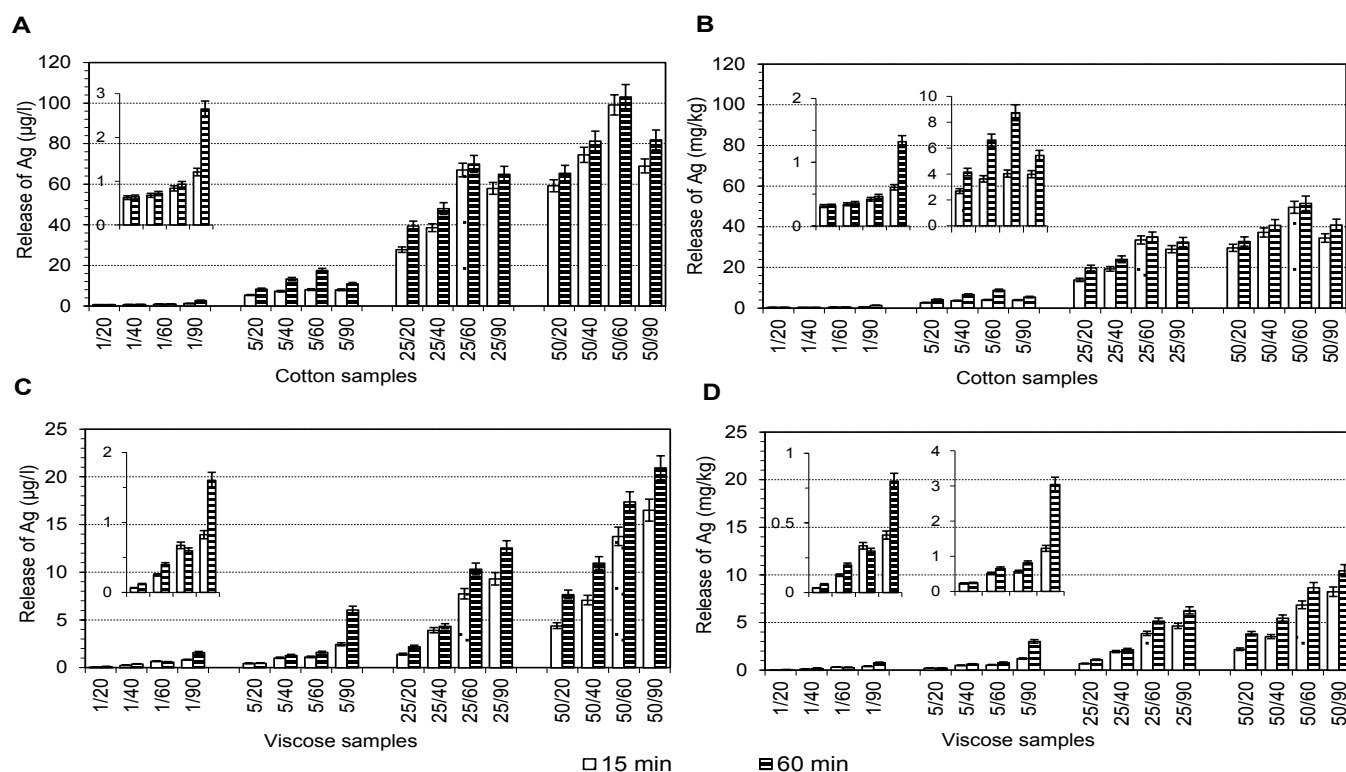
Figure 9: Ag release from cotton and viscose in µg/l (A and C) and mg/kg (B and D) at mass of textile to water-volume ratio of 1:500, contact time of impregnation 15 min and 60 min.

Samples	D. magna		V. fischeri	
	EC50 mg/l	TU	EC50 mg/l	TU
A - Cotton 50/60/90°C	0.033	30.53	1.380	7.25
B - Cotton 50/60/40°C	0.032	31.51	1.710	5.85
C - Cotton 50/60/60°C	0.028	35.17	1.160	8.62

Table 5: Toxicity of water solutions containing AgNPs toxicity for organisms.

observed for Ag nanoparticles and Ag ions seem similar. The present study results demonstrated that the Ag water solution samples revealed a toxic effect on *D. magna* and *V. fischeri*. Among the tested species, *D. magna* was most sensitive and revealed acute toxicity for low EC50 values. The low EC50 values obtained for *D. magna* were caused by their filter–feeding strategy leading to an effective nanoparticle uptake [29,55] found out that *D. magna* could retain AgNPs in their internal organs after ingestion (Table 5). Moreover, *D. magna* is frequently used in the nano–ecotoxicological tests because it is one of the organisms most sensitive to toxic chemicals. It also occupies the central position in the food chain [29,30,51,53,56]. As *Daphnia* is an element of the diet of other aquatic organisms (e.g. fish), it is an important link in the potential uptake and transfer of nanoparticles to higher organisms [29]. For that reason, a relatively high number of results concerning this species is described and published. The study of Binaeian et al. [57] showed that *V. fischeri* was also sensitive to the toxicity effects of Ag ions and nanoparticles and could be used as a biosensor of the acute nanoparticle toxicity. It was found out that the Ag ions were more toxic for *V. fischeri* than the Ag nanoparticles [50,57] discovered that the AgNPs were less toxic to bacteria than to aquatic organisms. The studies are consistent with the results obtained in this study (Table 1).

The EC50 values for Ag nanoparticles were 0.01, 0.36, 1.36, and 7.1 mg/l for crustaceans, algae, fish and bacteria, respectively [50]. The response of *V. fischeri* was less sensitive due to the physiological state of the bacteria. Small particles tend to show high toxicity to aquatic organisms. When the particle size is smaller than the cell wall pore (5–20 nm), they can easily penetrate the algal cell [58].

Conclusion

The study investigates the Ag release from textiles (socks available in the Polish market, cotton and viscose filled with Ag nanoparticles) into the washing solution under different conditions. The released Ag amount depended on a multitude of factors, such as test media (chemical composition, temperature and water volume), metal contents, or textile impregnation condition. Furthermore, the textile type and colour were the main parameters affecting the Ag release. The Ag concentration in the washing solution was 0.015–4.44 µg/l (socks) and 0.61–103 µg/l (cotton filled with AgNPs). The percentage of the total Ag released into water during one washing varied considerably among textiles (from less than 1 to 34%). In the presence of tap water, the released Ag load decreased from 6.82 to 1.35 mg/kg due to the AgCl and/or Ag_2CO_3 precipitation.

The bleaching process had a strong effect on the quality and speciation of Ag released in the washing process. For example, the Ag concentration in the washing solution changed from 0.8 µg/l to 12.9 µg/l and was higher by 20 times (white socks) and up to 170 times (black socks) when compared to washing in water without any oxidising agent. The washing of the nano–Ag–treated textiles may have potentially released both ionic and particle Ag forms because smaller AgNPs dissolved more rapidly than larger AgNPs. The situation is due to the larger fraction of surface atoms (higher specific surface area) in

smaller AgNPs or due to lower redox potentials of smaller AgNPs (in comparison with large particles). Furthermore, small particles tend to show high toxicity towards aquatic organisms. When the particle size is smaller than the cell wall pore (5–20 nm), they can easily penetrate the algal cell. The results of the present study demonstrated that the water solution containing Ag revealed a toxic effect on *D. magna* and *V. fischeri*. Among the tested species, *D. magna* was most sensitive and revealed acute toxicity for low EC50 values. The response of *V. fischeri* was less sensitive due to the physiological state of the bacteria. The information obtained in this study may be used to evaluate the potential risk to the ecological system posed by textiles from which AgNPs are released during their life cycle.

Acknowledgement

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