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Comparative study of leaching of silver nanoparticles from fabric and effective effluent treatment

Aneesh Pasricha^{1,a}, Sant Lal Jangra³, Nahar Singh¹, Neeraj Dilbaghi³, K. N. Sood²,
Kanupriya Arora¹, Renu Pasricha^{2,*}

1. Delhi Public School, Dwarka, New Delh-110078i, India. E-mail: ap1094@gmail.com

2. CSIR-National Physical Laboratory, New Delhi-110012, India

3. Department of Bio & Nano Technology, Guru Jambheshwar University of Science & Technology, Hisar, Haryana-125001, India

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Abstract

Nano silver (Ag_n) is employed as an active antimicrobial agent, but the environmental impact of Ag_n released from commercial products is unknown. The quantity of nanomaterial released from consumer products during use should be determined to assess the environmental risks of advancement of nanotechnology. This work investigated the amount of silver released from three different types of fabric into water during washing. Three different types of fabric were loaded with chemically synthesized Ag nanoparticles and washed repeatedly under simulated washing conditions. Variable leaching rates among fabric types suggest that the manufacturing process may control the release of silver reaching the waste water treatment plants. In an attempt to recover the Ag_n for reutilization and to save it from polluting water, the effluents from the wash were efficiently treated with bacterial strains. This treatment was based on biosorption and was very efficient for the elimination of silver nanoparticles in the wash water. The process ensured the recovery of the Ag_n leached into the effluent for reutilization, thus preventing environmental repercussions.

Key words: silver nanoparticles; leaching; eco-environment; effluent; SEM; TEM; AAS

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Introduction

Almost 50 years after Richard P. Feynman unveiled the revolutionary concept of nanotechnology, medical and engineering researchers have succeeded in manipulating these unique processes to enable novel applications in consumer products. Blinded by its efficiency, researchers, industrial producers and consumers have overlooked the potential environmental consequences.

Nano silver is the most common commercialized nanomaterial and is used in more than 200 products. Indeed, these consumer products (socks, bandages, underwear, storage boxes etc.) are surprisingly efficient in reducing odors and eliminating unwanted microorganisms (Durán et al., 2007; Kim et al., 2007; Lok et al., 2007; Morones et al., 2005; Panáček et al., 2006; Shahverdi et al., 2007; Sondi and Salopek-Sondi, 2004; Tian et al., 2003; Yoon et al., 2007). However, this involves a high risk of the leaching of Ag_n especially into water bodies. The size and chemical characteristics of these manufactured nanoparticles give them unique properties, which pose unique and unpredictable human health and environmental risks (Colvin,

2003; Chai, 2008).

Despite the growing commercialization of Ag_n , little is known about the environmental effects of the widespread use of products containing silver nanoparticles (Morris, 2007). While silver is known to be toxic to fish and aquatic organisms, recent scientific studies have shown that the nano form of silver is more toxic and can cause damage in new ways (Fahrenthold, 2008; Moore, 2006; Blaser et al., 2008). Exposures can occur both during use and during disposal. Even if the nanoparticle itself is not especially toxic, it increases the effectiveness of delivering silver ions to locations where they can cause toxicity. Ionic silver is highly toxic to aquatic organisms (McGeer, 2000; Ratte, 1999; Richards, 1981), and the United States Environmental Protection Agency (USEPA) has set water quality criteria values for silver in salt and fresh water at 1.9 and 3.4 ppb, respectively. The USEPA has also instituted a secondary drinking water standard for silver of 100 ppb.

The ubiquitous use of commercial products containing Ag_n could potentially compromise the health of many ecosystems. Antibacterial properties of nano silver come as a result of the way it acts as a catalyst, disabling the enzyme, or chemical lung, that bacteria need for their oxygen metabolism. Much like antibiotics, Ag_n does not

* Corresponding author. E-mail: pasrichar@mail.nplindia.ernet.in

^a The paper is part of the work submitted and selected for IRIS National Fair 2010.

distinguish between useful and harmful bacteria – it just kills any bacteria it comes into contact with, many of which are beneficial, even necessary, for our survival and the survival of other species. Toxicity and exposure data for Ag_n , however, is currently lacking (NNCO, 2006; Fahrenthold, 2007; Karn et al., 2003). Studies have demonstrated the toxicity of silver nanoparticles to bacteria, suggesting that the antimicrobial effects of silver may be detrimental to aquatic ecosystems (Kim et al., 2007; Morones et al., 2005; Panáček et al., 2006; Sondi and Salopek, 2004; Yoon et al., 2007). Therefore, it becomes increasingly important to characterize and quantify the silver released from commercial products.

This article investigates Ag_n release from different types of fabric into water as well as adsorption characteristics of the fabrics used. The amount of Ag_n in the fabric was quantified before determining the concentration of the silver released during repeated washing of the fabric with distilled water. Three different types of fabric were chosen based on the widespread industrial application of Ag_n .

It has been proven that fibers that contain silver nanoparticles in the core-part (inside the fiber) had no significant antibacterial activity (Yeo and Jeong, 2003). However, fibers that have silver nanoparticles in the sheath-part showed excellent antibacterial effects. Hence the loading process was undertaken to ensure the loading of Ag_n on to the sheath of the fibers. Scanning electron microscopy (SEM) was used as surface analysis tool to confirm the loading on the sheath of the fabrics. Yet another important aspect of nanotechnology is the ecotoxicological concern (Richard and Robert, 2008). The recovery of Ag_n , using a biotechnological approach involving bacteria, is of paramount importance to avoid environmental damage (Durán and Menck, 2001; Durán et al., 2007; Pal et al., 2007).

Very few reports on detecting or remediating rivers or industrial effluents from nanofactories have been published. Silver released from commercial clothing (socks) into water and its role in wastewater treatment plants has been studied by a few groups so far (Benn and westerhoff, 2008; Mueller and Nowack, 2008). A preliminary study with *Chromobacterium violaceum* by Duran et al. (2007) acting on textile effluent containing silver nanoparticles exhibited an efficient absorption of these nanoparticles (Dura'n et al., 2007). All the above mentioned reports uses bacteria that may be fatal to humans and have been reported to cause irreparable damage and are also immune to antibiotics.

Here in this report we have used two widely studied bacterias, *Bacillus subtilis* (441) and *Pseudomonas stutzeri* (10033) for the effectual effluent treatment of waste water to ensure that Ag_n does not reach the sewage disposal plants endangering the biomass and further reach the environment (aquatic and soil).

1 Materials and methods

1.1 Materials

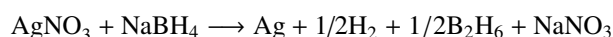
Silver nitrate (AgNO_3) and sodium borohydride (NaBH_4) were purchased from Sigma-Aldrich, nutrient agar and

nutrient broth were purchased from Himedia. All reagents were used as received without further purification.

Cotton, wool and nylon fabrics were used for loading of silver nanoparticles. De-ionized water (18 mega ohm resistivity) prepared from Millipore milli-Q element water purification system (USA) was used throughout the process. The bacterial cultures *Pseudomonas stutzeri* (MTCC 10033) and *Bacillus subtilis* (MTCC 441) were procured from Microbial Type Culture Collection, IMTECH, Chandigarh. These were maintained on nutrient Agar slants at 4°C by regular transfer.

1.2 Synthesis of Ag nanoparticles

Ag nanoparticles were synthesized chemically as the method described in the literature (<http://www.philasim.org/newmanual/exp29.pdf>). A 100-mL aqueous solution of 1.0×10^{-3} mol/L silver nitrate was mixed with a 300-mL aqueous solution of 2.0×10^{-3} mol/L sodium borohydride. Both solutions were prepared using Millipore water and these solutions were chilled to ice temperature before mixing. On mixing both solutions, Ag ions were reduced to form mono dispersed nanoparticles as a transparent sol in aqueous medium. The reaction is described in the following reaction:



The Ag solution thus formed was yellow in color and showed an absorption at 400 nm, which is characteristic of silver nanoparticles due to the excitation of surface plasmons (Selvakannan et al., 2004). The solution was stirred repeatedly whenever the color darkened (for approximately an hour) until it stabilized. At this point, the Ag nanoparticles solution was so stable that it did not change color for three months without any stabilizing agent. The aggregation state of the particles was observed with a UV-Vis spectrometer. The particle size and aggregation state of particles were further measured using the transmission electron micrograph.

1.3 Loading of silver nanoparticles on fabrics

All fabrics were washed, sterilized and dried before use. Experiments were performed on samples with maximum dimensions of 5 cm × 5 cm. The final filtrate of Ag nanoparticles (100 mL) obtained above was treated by ultracentrifugation for 5 min to get a uniform solution. To impregnate fabrics (5 cm × 5 cm), these were submersed in a conical flask (250 mL) containing the nanoparticle solution and kept overnight. Thereafter, they were shaken at 600 r/min for 4 hr and dried at 70°C. The quantity of silver nanoparticles incorporated in the cotton fabrics was measured by conducting atomic absorption spectroscopy (AAS) of the silver solution left after taking the fabrics out.

1.4 Washing of fabric

Fabrics were placed in 100 mL glass bottle with 50 mL of ultrapure water (millipore water). The bottles were agitated for either 60 min using a stirrer/ or centrifuged for 30 min at approximately 50 r/min. The time was chosen to

allow sufficient opportunity for the fabric to leach silver. The time is more representative of a “real world” washing machine cycle. Afterwards the fabrics were removed, excess water was wrung out into the glass bottle, and the fabrics were dried at 70°C. After drying, the fabric was placed in a new bottle for the next washing. Each fabric was washed at least 5 consecutive times.

1.5 Biosorption of Ag nanoparticles

Fresh 100 mL of silver solution was mixed with 0.5 g of bacterial biomass obtained after centrifugation of bacterial suspension grown on shaker at 37°C for 12 hr. The samples (Ag sol and the bacteria) were mixed on a shaker table at 45 r/min for 1 hr of contact time so as to allow adsorption to take place. The samples were thereafter filtered through a 0.4 or 0.45 μm membrane filters to remove any suspended biosolids. The filtrate was analyzed for total silver by AAS and the biomass was analyzed by SEM for verifying the adsorption of Ag by the bacteria. All the sets of experiments were performed in triplicate to ensure consistency in the results.

1.6 Characterization

The absorption spectrum of each solution was recorded in the range 190–1100 nm using UV 1800 Shimadzu UV spectrophotometer for 10 min after the completion of the reaction. Scanning and transmission electron microscopy (TEM) were used to confirm the presence of silver nanoparticles in the fabric material. Energy dispersive X-ray analysis (EDX, Oxford INCA250 energy, UK, or EDS) was performed to confirm the elemental presence of silver metal.

For characterization by high resolution transmission electron microscope (HRTEM), Tecnai G² F30 S-Twin (FEI; Super Twin lens with $C_s = 1.2$ mm) instrument operating at an accelerating voltage of 300 kV having a point resolution of 0.2 nm and lattice resolution of 0.14 nm was used. Program Digital Micrograph (Gatan) was used for image processing. For the imaging, the fabric wash water was first evaporated to concentrate the nanoparticles, thus increasing the probability of identifying them. A drop of the concentrated washwater was drop casted on the carbon coated copper grids for the TEM analysis.

Scanning electron microscopy was performed using

ZEISS EVO MA-10. The fabrics were used to check the loading of silver nanoparticles and selective areas with good contrast were sampled to record the images. EDS was conducted to ascertain the presence of silver.

Atomic absorption spectrometer (AAS) was performed to quantify the silver loading and leaching from the fabrics. The synthesized and concentrated solution of silver was used as a reference sample. The silver measurements were carried out at 328.1 nm wavelength and optimum conditions of air/acetylene using Analytic Jena make Vario-6. The reference standards (BND 505.01) solution of 5 mg/kg of silver was used for calibration of instruments after appropriate dilutions.

2 Results and discussion

Since silver is a good antibacterial agent and non-toxic in low quantities, it is an interesting material to be used in different kind of textile fibers. In this direction, three different types of fabric were chosen based on the widespread industrial application of Ag_n. These fabrics were loaded with silver nanoparticles in the method described above to ensure that the loading is in the sheath part of the fiber.

Many synthetic procedures for the silver nanoparticles synthesis are available, but a narrow and controlled size preparation seems difficult to obtain as the latter depends on the adjustment of the concentration of reacting chemicals and controlled reaction environment. To prepare the stable silver nanoparticles via the chemical reduction method, it is important to choose appropriate stabilizer and reducing agents. We tried a few methods given in the literature and settled on the borohydride reduction of silver nanoparticles at low temperature because of the almost uniform size distribution, ease of reaction and the formation of stable particles in aqueous solution without the use of any capping agent. The silver nano particles are stable upto two or three months and remains in zero-valent state, but at the same time there is a possibility of few unreduced silver ions left in the colloid during reduction. During the loading procedure, along with the Ag_n, theses unreduced ions can also get loaded onto the fabric. The unreduced Ag ions on exposure to air and repeatedly exposure to water converts partially into oxidized state. Hence there is a possibility of silver ions also getting released in wash water during the

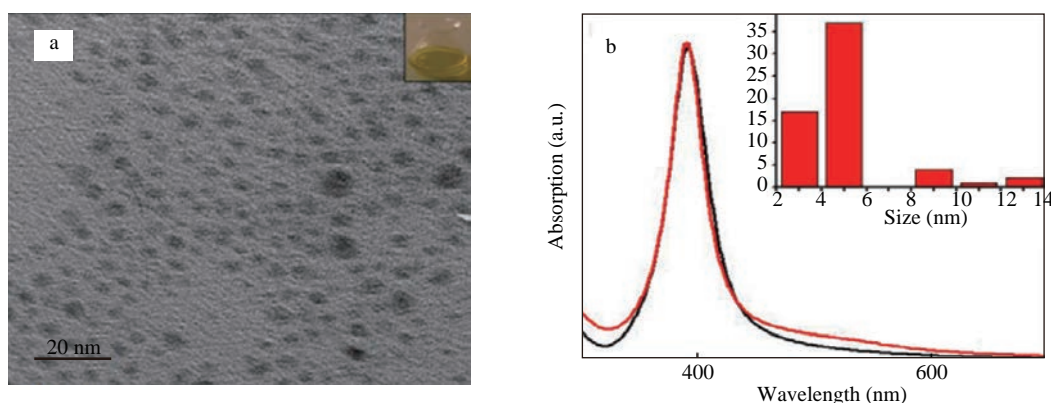


Fig. 1 (a) Representative TEM bright field image of the synthesized silver nanoparticles, inset shows the colloid formed on reduction, (b) UV-Vis spectra of as synthesized and concentrated Ag nanoparticles, inset shows the particle size distribution.

experiment and this can be taken up as a separate study. Figure 1 shows a representative TEM image corresponding to the sample of silver nanoparticles that are about 3–6 nm in diameter. The particles are spherical in shape and are fairly monodispersed. There are a few bigger particles, which may be due to agglomeration. As for the particle size distribution, the inset of Fig.1b shows that the diameter is (4 ± 2) nm.

2.1 Quantification of incorporated silver in fabrics

The impregnation or loading of Ag_n was different for different fabrics. AAS of the silver solutions prior to loading, and after the loading process, was conducted to quantify the amount of silver incorporation on the fabrics of the same size under the same experimental conditions. The results show that the concentration of as synthesized solution was 51.5 mg/L. After the loading, the AAS of the left over solution confirmed the decrease in the amount of silver. It was assessed to be 31.068% of the initial concentration (51.5 mg/L) for cotton, 10.097% for wool and 10.679% for nylon. The results of the AAS are summarized in Table 1.

2.2 SEM confirmation

The impregnation of silver nanoparticles in the cotton, wool and nylon fabrics was also verified by SEM-EDS. Figure 2 shows the SEM images of the fabrics before loading the nanoparticles. We can notice the clean sheaths of the intertwined fabrics. Figure 3 is the representative micrographs of the cotton, nylon and woolen fabrics loaded with Ag_n . Figure 3 shows the low and high magnification images of Ag_n impregnated cotton fabric, nylon fiber and woolen fabric respectively along with their corresponding EDS and its quantified data. The silver nanoparticles loaded on the fibers are marked with arrows. The presence of the silver peak was also confirmed by EDS (shown along with each SEM image) of the corresponding fabric. The carbon and oxygen peaks in the EDX analyses can be attributed to the surrounding fabric material. Particles of agglomerated silver with varying diameters exist within the three types of fabrics. The comparison of the micrographs with Fig. 1 indicates that the silver nanoparticles in these SEM micrographs do not appear nearly spherical, but are irregularly shaped and much bigger due to aggregation of the nanoparticles.

Table 1 Percentage loading and leaching of Ag nanoparticles from different fabrics

Fabric	Loading of Ag (%)	Leaching after 1st wash (%)	Leaching after 2nd wash (%)	Leaching after 3rd wash (%)	Cumulative leaching (%)
Cotton	31.068	10.000	1.590	0.804	12.394
Nylon	10.679	6.009	4.492	3.272	13.773
Wool	10.097	22.155	1.704	1.306	25.165

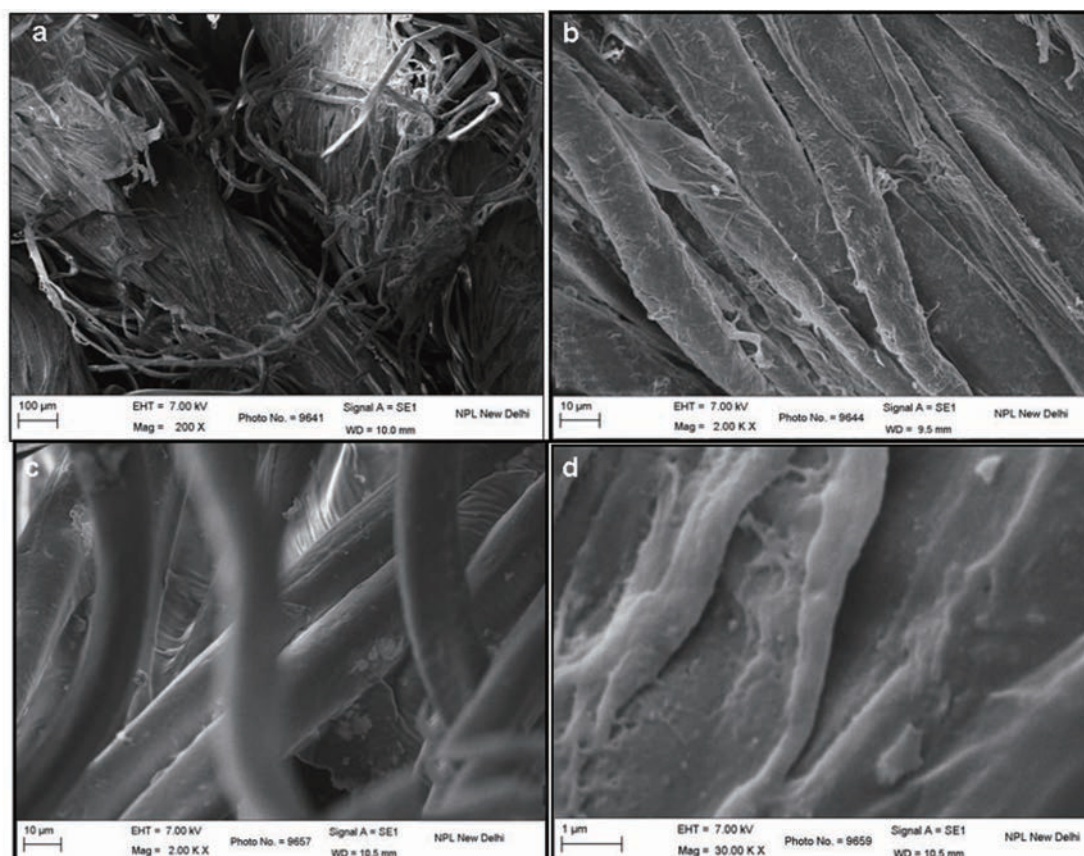
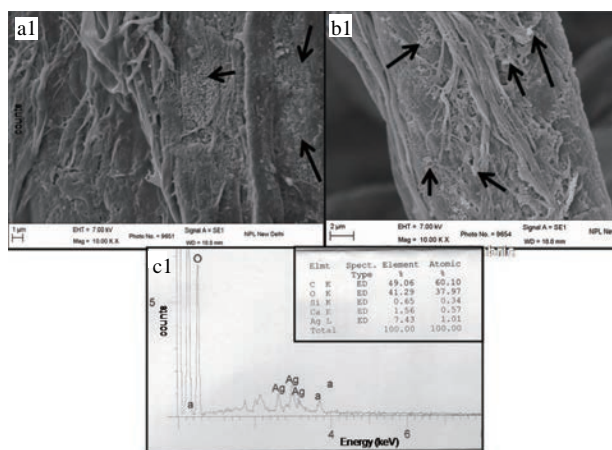
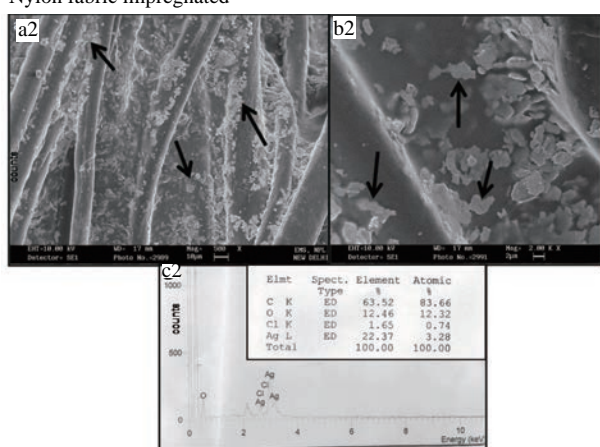


Fig. 2 SEM micrograph of cotton fabric (a), (b) and woolen fabric (c), (d).

Cotton fabric loaded



Nylon fabric impregnated



Woolen fabric impregnated

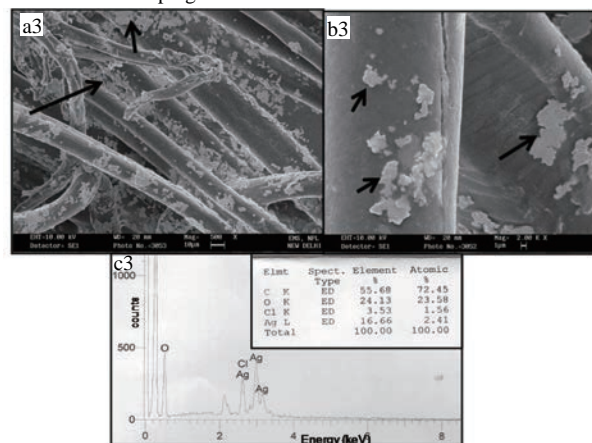


Fig. 3 Low (a) and high (b) magnification SEM micrographs of the cotton fabric loaded, nylon fabric impregnated, woolen fabric impregnated with silver nanoparticles, marked with black arrows, with the EDS spectrum of cotton fabrics (c1), nylon fabrics (c2) and woolen fabrics (c3) containing silver nanoparticles and its quantified results.

2.3 Release of silver into wash water

All the three fabrics detectably leached silver into the millipore wash water. The fabrics previously loaded with silver nanoparticles were washed three times (simulating the conditions inside a washing machine). Table 1 shows the particles released in each wash by the fabrics. It can be seen that silver was steadily released throughout

the washes. Table 1 also presents the cumulative silver released during three sequential washes of the samples. After three times washes, 12.144% of silver nanoparticles were released by cotton fabric, 14.000% were released by wool and 24.442 % were released by nylon fabrics.

The fabrics were still releasing significant amounts of silver after the second wash but none of the fabrics leached detectable silver after the third wash. The silver content in the 50 mL wash water (from the wash of each fabric) varied from fabric to fabric and also for each washing cycle (ranged from 0.77 to 1.94 mg/L). A comparison of fabric based on the amount of silver leached relative to the silver content of the fabric (Table 1) suggests that the fundamental differences in the type of fabric and in the amount of loading control the amount of silver that is released into the wash water. For example, cotton contained relatively large amounts of silver (16 mg/L), and released only small percentages (12.144%, i.e., 1.943 mg/L) of its total silver into the wash water, while nylon released 14% and wool released 24% of its silver content in three consecutive washes. Additionally, the fabrics release their silver into the wash water at different rates. Cotton released the most silver during the first wash, while nylon steadily increased its release of silver throughout subsequent washes. These data suggest that the various fabrics types have different longevities in which the silver continues to function as an antimicrobial agent over a long period of time. It would be interesting to study the durability of antimicrobial activities of commercial products after subsequent washes.

2.4 Characterization of the wash water for silver nanoparticles

TEM analysis of the colloids in the wash water of fabrics presented as Fig. 4 indicates the presence of silver material with diameters of 8–20 nm. These particles are bigger than the original synthesized nanoparticles. A few are irregularly shaped, like the particles in the SEM image of impregnated fabrics. The increase in size may be due to the agglomeration. There is a possibility that some of the silver released might be in ionic form as explained earlier.

2.5 Treatment of effluent from fabric water washes

The effluent thus obtained was treated with *Pseudomonas stutzeri* and *Bacillus subtilis*. The bacteria were grown in a nutrient broth medium and the samples (bacteria and Ag nanoparticles) were allowed to mix on a shaker table at 45 r/min for 1 hr of contact time so as to allow ample time for adsorption to take place. After the treatment, the bacteria treated effluent was filtered through a 0.4 or 0.45 μ m membrane filter to remove any suspended biosolids. The filtrate was analyzed for total silver by AAS and also by UV-Vis spectroscopy. The bacteria after treatment were also studied using the SEM, to note any change in morphology.

The entire study of the synthesis of Ag nanoparticles, the loading on different fabrics, leaching from fabrics on washing and thereafter the effluent treatment of wash water was supported by extensive UV-Vis spectroscopy at every step. Figure 5a shows the comparative intensities of the

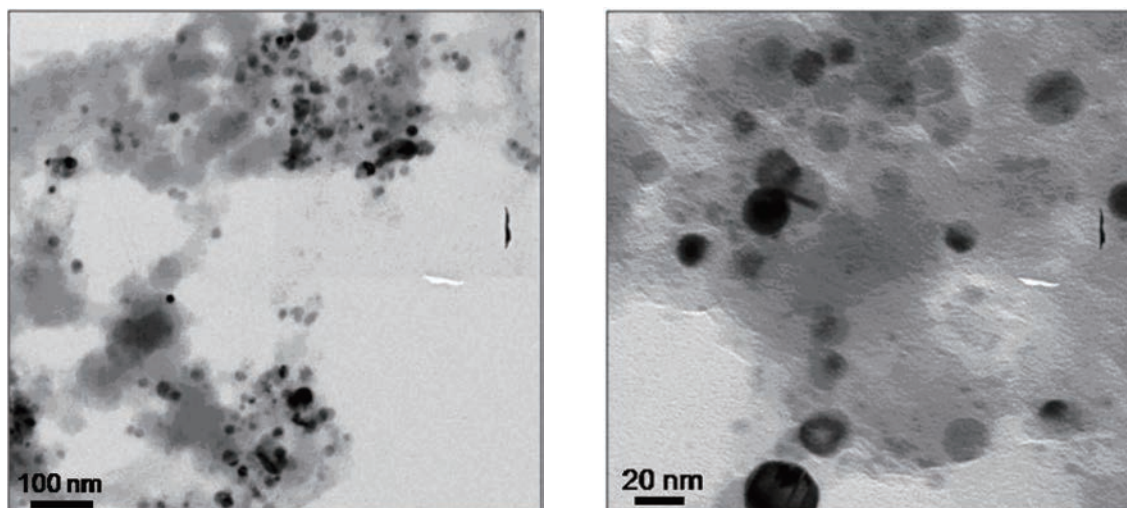


Fig. 4 TEM image of colloidal material from cotton fabric wash water.

UV-Vis spectra peaks of the Ag solution left after the loading of Ag nanoparticles on to the different fabrics. The appearance of an additional peak was observed in the case of wool. This may be due to the agglomeration of nanoparticles left in the solution due to the treatment with fabric. The decrease in the intensity of the peak at about 400 nm is a clear indication of the loading of Ag nanoparticles on the fibers.

The leaching of the Ag nanoparticles was observed using an AAS study performed on the wash water samples after each wash. The UV-Vis spectrum of the wash water solution was also analyzed. The results are presented as Fig. 5b for the three kinds of fabric. The peak position confirms the presence of silver in wash water. Figure 5c shows the trends in the silver released in the wash water after each wash for cotton (curve C), nylon (curve N) and

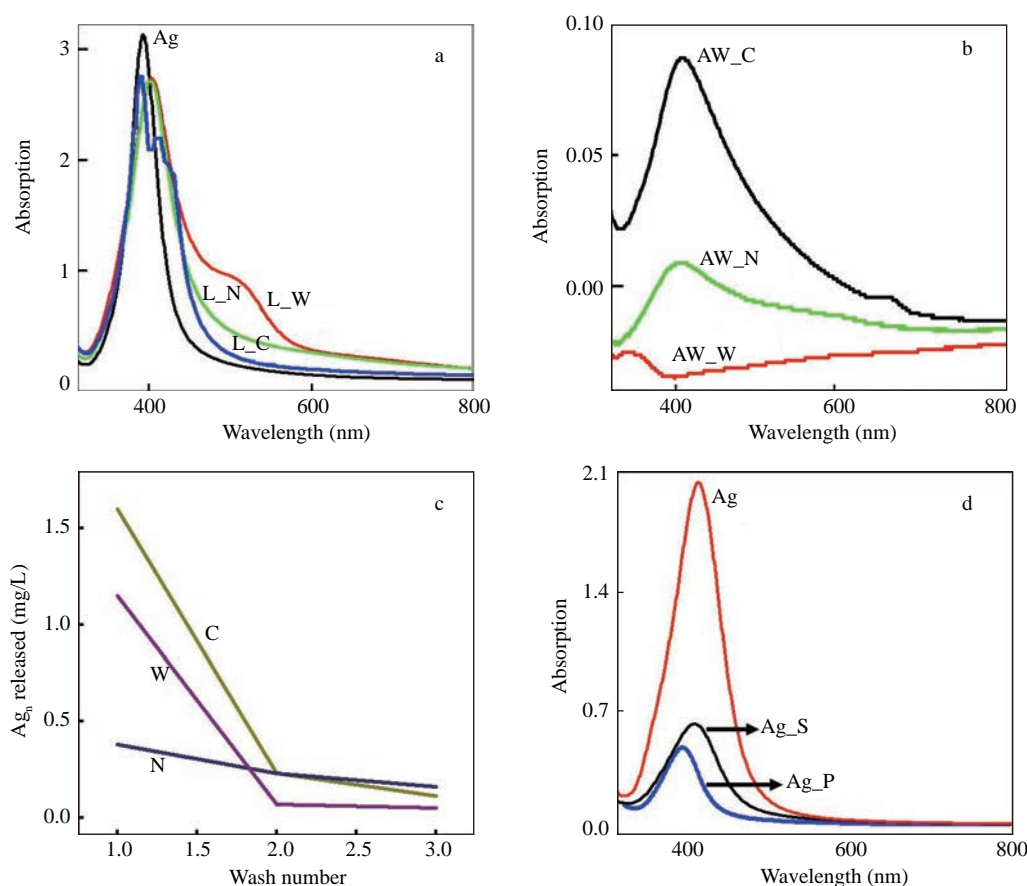


Fig. 5 (a) UV-Vis spectra of the Ag solution left after loading onto different fabrics. Curve Ag: absorbance spectra of as synthesized Ag nanoparticles, spectra of solution left after loading on woolen fabric (L.W), cotton fabric (L.C) and nylon fabric (L.N), (b) UV-Vis spectra of the effluent from cotton (AW.C)/wool (AW.W)/nylon (AW.N) fabric water washes, (c) cumulative mass of silver released from the fabrics in three consecutive washings in distilled water from cotton (C), wool (W) and nylon (N), (d) UV-Vis spectra of the Ag solution before treatment (Ag) with bacteria and after treatment with *Bacillus subtilis* (441) (Ag-S)/with *Pseudomonas stutzeri* (10033) (Ag (Ag-S)-P).

wool (curve W). It is clear from the graph that nylon shows a uniform trend for the release of Ag_n , whereas in the case of cotton and wool, we see a decrease in the rate of release after each wash cycle.

The effluents obtained from the cotton fabric wash process were efficiently treated with *Bacillus subtilis* (441) and *Pseudomonas stutzeri* (10033). This treatment was based on biosorption and is very efficient for the elimination of silver nanoparticles remaining in the wash water. Figure 5d shows the UV-Vis spectrum of this effluent before and after the treatment with bacteria. Curve Ag corresponds to the UV-Vis absorbance peak of the synthesized silver and curves Ag_S and Ag_P correspond to the absorbance spectra for the effluent, after treatment with bacteria. An intensity decrease of the plasmon resonance (400 nm) was observed after the wash water was treated with bacteria, indicating a reduction in the concentration of silver nanoparticles in the effluent. This reduction in the peak intensity is due to the capture of these particles by bacteria, as verified by SEM/EDS also. The results are presented later. The SEM/EDS, AAS and the UV absorbance studies confirm the biosorption of silver nanoparticles by bacteria, thus implying that the presence of these bacteria is effective for the treatment of effluents.

As a confirmatory test, the effluent was mixed with a culture medium without bacteria and was filtered. No change in the absorption value was observed. This result verified that the silver nanoparticles were not retained in the filter in the absence of bacteria.

Figure 6 shows the SEM micrograph of bacteria *Bacillus subtilis* (441) cells after bacterial treatment of the effluent with silver nanoparticles. Biosorbed Ag_n can be seen in the micrograph. Morphological changes of the cells from

small rods (inset) to curved, coiled structures were observed. This change was only observed in cells loaded with Ag_n . The EDS of the region with irregularly shaped cells shows the presence of Ag. A similar result was observed by Feng et al. (2000) when they used *C. violaceum* in the presence of silver nanoparticles.

AAS analysis of the effluent after treatment with the bacteria *Bacillus subtilis* showed a reduction in the concentration of silver by 70%, demonstrating that the silver nanoparticles were effectively removed from the effluent.

The recovery of the silver material thus adsorbed could be through the digestion of biomass. This method can be used in the efficient recovery of the silver leached into effluent, avoiding damage on the eco-environment. The recovery can be taken up as a separate study.

3 Conclusions

We present a comparative study depicting the loading of Ag_n on to different fabrics (cotton, wool and nylon). The fabrics were treated to multiple washing sessions after Ag_n impregnation to analyze the amount of silver leached into the wash water. It can be inferred from the study that fundamental differences in the types of fabric control the amount of silver that is loaded on to fabric and also released into the wash water. Additionally, the fabrics release their silver into the wash water at different rates.

The wash water (effluent) was treated with bacteria. This treatment was based on biosorption and can be used for the efficient elimination of silver nanoparticles remaining in the wash water, preventing damage to the environment. The silver nanoparticles obtained by digestion of biomass can be reused for the impregnation of other fabrics, avoid-

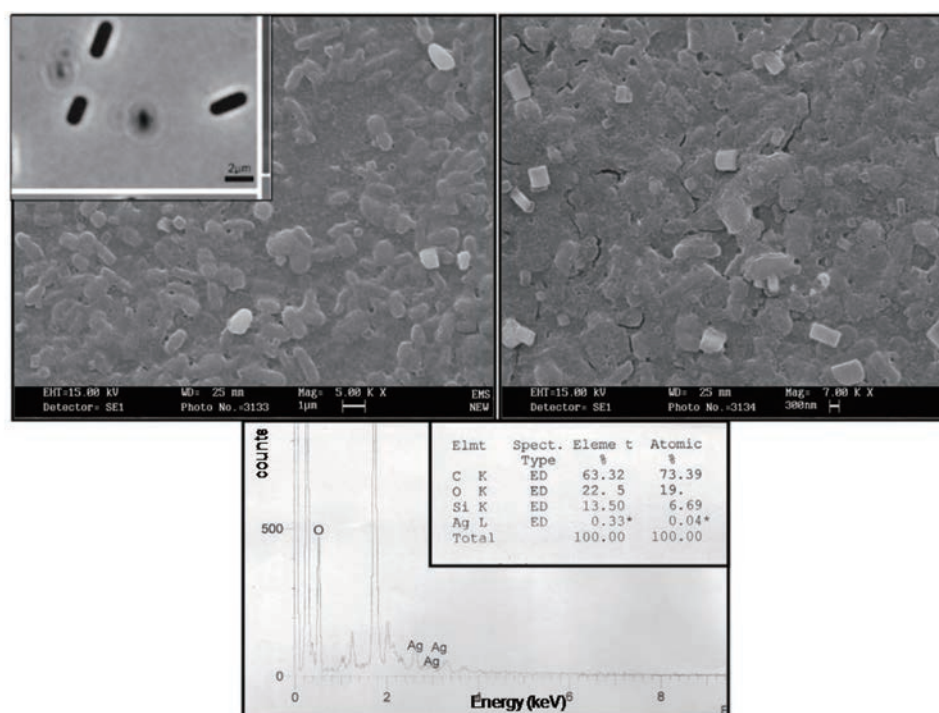


Fig. 6 EDS spectrum showing the presence of silver and the SEM micrograph (low and high magnification) of the *Bacillus subtilis* (441) after effluent treatment. Inset shows the untreated bacteria.

ing damage to the eco-environment. The study further opens up new avenue to be explored in this field.

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