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1. Introduction

The textile industry in developed countries is confronting the world’s marketing conditions and competitive challenges which are driving towards the development of advanced, highly functional textiles and textiles with higher added value. The conventional textile finishing techniques are wet chemical modifications where water and rather hazardous chemicals are used in large quantities and wastewaters need to be processed before discharging effluent, whereas the most problematic factor are ecological impacts to the environment and effects to human health. The increasing environmental concerns and demands for an environmentally friendly processing of textiles leads to the development of new technologies, the use of plasma being one of the suitable methods [1]. Plasma technology is an environmentally friendly technology and a step towards creating solid surfaces with new and improved properties that cannot be achieved by conventional processes [2]. Plasma is the fourth state of matter. It is a gas with a certain portion of ionized as well as other reactive particles, e.g. ions, electrons, photons, radicals and metastable excited particles. Several types of plasma are known; however, only non-equilibrium or cold plasma is used for the modification of physical and chemical properties of solid materials such as textiles. Chemically reactive particles produced at a low gas temperature are a unique property of cold plasma; hence, there is minimal thermal degradation of a textile substrate during the plasma processing [3]. Cold plasma is a partially ionized gas with the main characteristic of a very high temperature of free electrons (typically of the order of 10,000 K, often about 50,000 K) and a low kinetic temperature of all other species. The average energy of the excited molecules is usually far from the values calculated from the thermal equilibrium at room temperature. The rotational temperature, for instance, is often close to 1000 K, while the vibrational temperature can be as
high as 10,000 K, although the kinetic (translation) temperature is close to room temperature. Furthermore, the dissociation fraction is often several percent, which is orders of magnitude larger than that calculated from thermal equilibrium at room temperature. This also applies to the ionization fraction; although this is often much lower than the dissociation fraction. Plasma with such characteristics readily interacts with solid surfaces, causing reactions that would otherwise occur only at elevated temperature of the solid material. For this reason, non-equilibrium plasma represents an extremely powerful medium for modification of the surface properties of solid materials. A medium of particular interest is weakly ionized highly dissociated oxidative plasma that can be sustained in high frequency discharges in oxygen, air, carbon dioxide, water vapor, and mixtures of these gases with a noble gas. Such plasma has been successfully utilized in an extremely wide range of applications from nanoscience to fusion reactors. Plasma is used for synthesis of nanostructures with interesting properties, removal of thin films of organic impurities, selective etching of composites, sterilization, passivation of metal, ashing of biological materials, etching of photoresists, functionalization of polymers, and conditioning of tokamaks with carbon walls [4-9].

The choice of discharge parameters is determined by the requirements of each particular application. For selective plasma etching, for instance, extremely aggressive plasma is needed; thus, it is created with powerful generators at a moderate pressure (where the O density is the highest) in pure oxygen or in a mixture of oxygen and argon. For treatment of delicate organic materials, on the other hand, weak plasma performs better, since aggressive plasma would destroy organic material in a fraction of a second. Therefore, extremely delicate organic materials are rather treated in an afterglow or in plasma created at low pressure and with a low-power generator. Water vapor is sometimes used instead of oxygen. The advantages of using plasma are ecological and economical. Moreover, the textiles subjected to the treatment are modified without an alteration of the bulk properties. Unlike wet chemical processes, which penetrate deep into the fibers, plasma produces no more than a surface reaction, the properties given to the material being limited to the surface layer of a few nanometers [10]. The modification of textile substrates using plasma enables different effects on the textile surfaces from the surface activation to a thin film deposition via plasma polymerization. In the first stage of the treatment, plasma reacts with the substrate surface where active species and new functional groups are created, which can completely change the reactivity of the substrate [11]. The changes in the surface morphology of fibers can be induced by plasma etching process where the nano- or micro-roughness of fibers is formed [12]. The nanostructured textile surfaces have a higher specific surface area, which leads to new or improved properties of the treated surface, i.e. increased surface activity, hydrophilic or hydrophobic properties, and increased absorption capacity towards different materials, i.e. nanoparticles and nano-composites [13-18].

When researching the deposition of nanoparticles onto different substrates, it is important to understand the adhesion of particles, which is dependent on the interaction mechanism with a material. The mechanism of nanoparticle adhesion has not been completely explained yet, since there are many different opinions among the theorists on the subject. Thus, it is generally considered that attractive forces and chemical bonds play an important role in the
adhesion of particles [19]. The physical or mechanical adhesion of nanoparticles mostly occurs due to van der Walls or electrostatic forces, while the chemical adhesion of particles is a consequence of ionic, covalent, metallic and hydrogen bonds [20]. Moreover, the nanoparticles can penetrate into certain parts of the substrate, such as pores, holes and crevices, and they lock mechanically to the substrate. This adhesion mechanism, which is called mechanical interlocking, has been solved from the perspective of surface roughness effects [21]. Since plasma causes etching of the fibers and leads to an increase of the surface roughness higher adhesion properties towards metal or ceramic particles onto substrates can be achieved [22-30]. The adhesion of TiN (titanium nitride) onto PP (polypropylene) and PC (polycarbonate) was increased after a modification of substrates with argon low-pressure plasma [31]. The roughness after plasma treatment increased from 15 nm to 17 nm for PP and from 12 nm to 30 nm for PC. Consequently, contact angles decreased from 95° to 59° for PC and from 87° to 35° for PP. The surface modification of polyethylene terephthalate (PET) polymer was created by oxygen and nitrogen plasma at different treatment times [32]. The surface of PET polymer was modified in order to achieve improved attachment of fucoidan, which is a bioactive coating with antithrombogenic properties. The attachment of fucoidan was improved by oxygen plasma treatment, especially due to the surface roughening. The adhesion work, the surface energy and the surface polarity of PA6 (polyamide-6) fibers were increased by dielectric barrier discharge (DBD) treatment in helium at atmospheric pressure. Furthermore, a new structure was observed at the nanoscale, with an increased roughness and a larger surface area, favoring the adsorption [33]. The self-cleaning and UV protective properties of PET fibers were drastically improved after a modification of PET fibers with oxygen plasma and loading of TiO₂ prepared by an aqueous sol-gel process [34]. Cotton also showed self-cleaning properties after RF plasma and TiO₂ treatment [35]. TiO₂ on textile substrates is also used for a biomedical application to improve antimicrobial effectiveness of the fabric [36]. By using oxygen radiofrequency plasma at a higher power input, the roughness of fibers increased and likewise the adhesion of TiO₂ onto treated fabric. Treatment of PA and PET with corona plasma increased the adhesion of colloidal silver which affected the antifungal protection of the fabrics [37]. The quantity of silver on plasma-treated fabric was three times higher than on untreated fabric.

Preparation of metal nanoparticles also enables the development of new biocides. Due to their large surface area and ability to detain moisture, the textile materials are an excellent environment for a microorganism growth. Microorganisms can cause milder, aesthetic unpleasantness to serious health related problems. Textile materials with an antimicrobial effectiveness are used for medical, military and technical textiles, textiles for sports and leisure and bedding. At nanotechnology researches in textiles, different forms of silver were used, such as metal silver nanoparticles, silver chloride (AgCl) and composite particles of silver and titanium dioxide (Ag-TiO₂) [3, 24, 25, 27, 38-47]. In the case of antimicrobial efficiency, the surface coating of nanosilver on titanium dioxide maximizes the number of particles per unit area in comparison with the use of an equal mass fraction of pure silver [48,49]. Different methods have been used for the deposition and loading of silver nanoparticles onto synthetic and natural textiles, i.e. sonochemical coating, sol-gel process, dip-coating, pad-batch and exhaustion method, the use of nanoporous structure of cellulose fibers as a nanoreactor.
for *in situ* synthesis of nanoparticles and plasma sputtering process [3, 27, 48-54]. The possibility of loading nanoparticles using exhaustion method started recently [55]. The exhaustion method is the best process for uniform distribution of nanoparticles and is especially appropriate to be used when the simultaneous application of nanoparticles and dye onto fabric is performed, and dyed and antimicrobial effective fabric is achieved at the same time [3, 24, 25, 27]. Depending on the desirable functionality of a functionalized fabric, a treating bath may contain only dye, dye and silver nanoparticles or silver nanoparticles alone. An exhaustion method for loading of silver nanoparticles onto textile substrate was also used on silk fibers [54]. In that research, different concentrations of colloidal silver were used (10, 25, 50 and 100 ppm) and the effect of medium pH on the silver nanoparticles uptake on the fibers was studied. The antimicrobial effectiveness of functionalized fibers was better for samples with higher silver concentration and for samples treated in a medium with a lower pH. Also the use of salt (NaCl) improved a uniform distribution of silver particles on the fibers’ surface which consequently improved antimicrobial effectiveness of fabrics. A difference between pad-dry-cure and exhaustion method on adhesion and antimicrobial activity of fabrics was performed with commercial silver nanoparticles and a reactive organic-inorganic binder [45]. Results revealed that using the same initial concentration of silver, the pad-dry-cure method resulted in a much lower quantity of adsorbed silver nanoparticles in comparison to the exhaust method. Another possible method for applying silver onto textiles is plasma polymerization method where surface of textile is functionalized with nanostructured silver film by magnetron sputtering [56].

When dealing with modification of textiles by silver it is important to know how the functionalization will affect the color change of fabric. A reflectance (UV/VIS) spectrophotometry is one of the methods to be used when detecting or controlling the presence of silver nanoparticles in a solution or on a textile substrate. It is a direct measure that the abundance of silver is in the topmost layer of the textile fabric [30]. The instrument analyzes the light being reflected from the sample and produces an absorption spectrum. Some of the electrons in the nanoparticles are not bound to the selected atom of silver, but are forming an electronic cloud. Light falling on these electrons excite the collective oscillations, called surface plasmons. The resonance condition is established when the frequency of light photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei. Surface plasmon resonance is the basis of many standard tools for measuring adsorption of material onto planar metal (typically gold and silver) surfaces or onto the surface of metal nanoparticles. It is the fundamental principle behind many color-based biosensor applications. As a result of the particles growth, an intense absorption band at 400 nm to 415 nm caused by collective excitation of all free electrons in the particles was observed [57]. Increase in diameters of the nanoparticles from 1 to 100 nm induces a shift of the surface plasmon absorption band to higher wavelength [50, 57-59]. That means that the size of nanoparticles is defined by their optical response, therefore by that the color that can be seen [50, 60]. Loading of colloidal silver nanoparticles onto bleached cotton fabric caused yellowish coloring of fabric with absorption maximum at 370 nm [24, 30]. The evaluation of color changes of textiles modified by silver nanoparticles was also determined in CIELAB color space [60]. Loading of colloidal silver nanoparticles in concentration of 10 ppm in-
duced very small, eye insensitive, color change ($\Delta E^* < 1$) to the fabric. When colloidal silver nanoparticles in concentration of 50 ppm were loaded, the color change of fabric was obvious ($\Delta E^* = 15.09$). Loading of silver onto textiles before or after dyeing also causes color changes; however the changes are not as extensive as with the white fabric. When colloidal silver was loaded before dyeing, the color change was $\Delta E^* = 1.44$ and when loaded after dyeing, the color change was $\Delta E^* = 2.73$. Color changes of textiles can be also induced by plasma treatment. When plasma is used for a modification of cotton to improve its hydrophilicity, then cotton has a better dyeability and consequently deeper coloration [61]. Also, a raw cotton fabric can be bleached by using ozone plasma [62]. The whiteness index (CIE WI) of fabric was even higher after plasma treatment than after peroxide bleaching (CIE WI $O_3 = 95.3$; CIE WI $H_2O_2 = 94.5$).

Since the modification of substrates by plasma improves the adhesion of metal nanoparticles onto substrates than it is no surprise that plasma modification of textiles has a special significance when applying silver nanoparticles. The chapter presents the influence of plasma treatment on loading capacity of cotton toward different forms of nanosilver. Exhaust dyeing process was used for loading of nanosilver onto plasma-treated cotton, which represents a new approach to textile finishing in achieving multifunctional textile properties.

2. Experimental setup and methodology

Low-pressure plasma of different working gases and air atmospheric corona plasma were used for a modification of textiles. Untreated and plasma-treated textile substrates were additionally modified by loading of silver nanoparticles during dyeing process. Morphological, chemical and physical properties of plasma-treated textile substrates were studied using microscopy (SEM), spectroscopy (XPS) and measuring of the breaking strength and elongation of textiles. The quantity of adsorbed silver was determined using mass spectrometry (ICP-MS), while the antibacterial efficiency of functionalized textiles was determined using microbiological tests.

2.1. Plasma modification of textiles

Cotton substrates were modified using different plasma systems, i.e. atmospheric air corona plasma [63-65] and low-pressure inductively coupled radiofrequency (ICRF) discharge plasma of different working gases, water vapor [3, 26, 66, 67] and tetrafluoromethane [27], respectively. ICRF plasma is particularly suitable for treatment of delicate materials with a large surface for the following reasons: the neutral gas kinetic temperature remains close to the room temperature; the plasma-to-floating potential difference is small; the density of neutral reactive particles is large; and extremely high treatment uniformity is achieved. The use of low-pressure plasma is a contemporary technological process, not yet fully applied in textile industry due to its discontinuous process. For a continuous, on-line processing interfaced to a conventional production line the use of corona atmospheric pressure plasma is recommended. Furthermore, the corona plasma treatment also introduces new functional groups onto fi-
bers surfaces, produces surface cleaning and etching effect of treated textiles. The comparative research of corona plasma treatment of polyester was presented as well [24].

2.1.1. Low-pressure plasma treatment

A RF generator with a nominal power of 5 kW and a frequency of 27.12 MHz was applied. The power absorbed by plasma, however, was much smaller due to poor matching and was estimated to about 500 W. The discharge chamber was a cylindrical Pyrex tube with a diameter of 27 cm and a length of 30 cm. Cotton fabric was put onto a glass holder mounted in the center of the discharge chamber. After closing the chamber the desired pressure of 0.4 mbar was achieved by a two-stage rotary pump with a nominal pumping speed of 65 m³/h. The pressure was fairly stable during the experiment. Although the ultimate pressure of the rotary pump was below 1 Pa, the pressure remained much higher at 40 Pa. The source of water vapor was the cotton fabric itself. When tetrafluoromethane was used as a working gas, it was leaked into the chamber in order to obtain a pressure of about 100 Pa, the pressure where plasma is most reactive. By switching on the RF generator, the gas in the discharge chamber was partially ionized and dissociated, starting the plasma treatment of the fabric. The plasma treatment time was 10 s in both cases. The schematic diagram of low-pressure RF plasma reactor is presented in Fig. 1.

![Figure 1. Schematic diagram of low-pressure RF plasma reactor](image)

2.1.2. Atmospheric plasma treatment

Textile samples were treated in a commercial device, Corona-Plus CP-Lab MKII (Vetaphone, Denmark) (Fig. 2). Samples (270 × 500 mm²) were placed on a backing roller (the electrode roll covered with silicon coating), rotating at a working speed of 4 m/min. The distance be-
tween electrodes was adjusted with air gap adjusters at both sides of the electrode to 2 mm. Corona discharge was generated within the air gap between the electrode and backing roller. The power was 900 W and the number of passages was set to 30.

Figure 2. Picture of atmospheric corona plasma reactor and a detail of treating area shown in a red circle

2.2. Morphological, chemical and physical properties of untreated and plasma-treated textiles

2.2.1. X-ray photoelectron (XPS) analysis

Information on the chemical composition and chemical bonds of surface atoms of untreated and plasma-treated textile samples was obtained with XPS analysis. During the XPS analysis, a sample is illuminated with monochromatic X-ray light in an XPS spectrometer and the energy of emitted photoelectrons from the sample surface is analyzed. In the photoelectron spectrum, which represents the distribution of emitted photoelectrons as a function of their binding energy, peaks can be observed that may correspond to the elements present on the sample surface up to about 6 nm in depth. From the shape and binding energy of the peaks within XPS spectra, the chemical bonding of surface elements was inferred with the help of data from the literature.

2.2.2. Scanning Electron Microscopy (SEM)

The morphological surface properties of fibers and their changes after plasma treatment were studied using scanning electron microscopy (JEOL SEM type JSM-6060LV). All samples were coated with carbon and a 90% Au/10% Pd alloy layer.
2.2.3. Dynamometer tensile testing

Breaking strength and elongation of untreated and plasma-treated fabrics were analyzed according to the ISO 2062:1997 standard. Instron 6022 was used for this purpose. 100 mm samples of cotton yarn were analyzed using a pre-loading of 0.5 cN/tex and a speed of 250 mm/min. Samples were conditioned according to the ISO 139 standard. Tensile stress (cN/dtex) and elongation ε (%) are the mean values of the measured tensile strength and the elongation of 10 specimens, respectively, in the warp and in the weft directions.

2.3. Modification by dyeing and nanoparticles

2.3.1. Nanoparticles

For a research three different types of silver nanoparticles were used: silver nanoparticles of known dimensions (Ames Goldsmith Inc.), commercial form RucoBac AGP (Rudolph Chemie) and laboratory synthesized colloidal silver nanoparticles. Silver nanoparticles of known dimensions was medium density mono-dispersed 30 nm silver powder (Silver Nano Powder NP-30) and high density mono-dispersed 80 nm silver powder (Silver Nano Powder NP-80) [68]. The powdered silver nanoparticles are namely intended for a fine line printing (Ink-jet printing) and for electronics use. Because of their purity and known size they are very suitable and important for studies of adhesion to textile materials [69]. The initial concentration of silver powders in the dyeing baths was 20 mg/l. Commercial form of silver nanoparticles RucoBac AGP is a hygienic finish for all fiber types. It is a highly concentrated hygiene and freshness system complying with the Oeko-Tex® standard 100. RucoBac AGP is a nano-dispersion of titanium dioxide (TiO₂) as the carrier of the active component silver chloride (AgCl) [70]. The recommended concentration of RucoBac AGP is 0.2–0.5%. Laboratory synthesized colloidal silver nanoparticles were made by a reduction of silver salt in an aqueous solution at room temperature. An amount of 25.5 mg of AgNO₃ was dissolved in 750 ml of bi-distilled water, and argon gas was introduced into the solution for 30 min. The reduction was performed with 375 mg of NaBH₄ under constant stirring. The solution was kept under an argon atmosphere for another hour [71].

2.3.2. Dyeing of cotton samples

2.3.2.1. Dyeing with reactive dyes.

Exhaust dyeing with or without the addition of silver nanoparticles [3, 27, 72] was performed on untreated and plasma-treated cotton samples. The dye solutions were separately prepared using two different dyeing concentrations: blank (dyeing without dyestuff) and 0.05% on weight of fabric (owf) of Cibacron Deep Red S-B in liquor ratio 20 : 1. Dyeing baths contained 30 g/l of salt (Na₂SO₄ anhydrous) and 8 g/l of sodium carbonate (Na₂CO₃ anhydrous). After the dyeing process, rinsing with distilled water was performed and neutralization with 1 ml/l of 30% acetic acid (CH₃COOH). As a soaping agent 1 g/l of CIBAPON R was used.
2.3.2.2. Vat dyeing procedure

Vat dyeing was performed on untreated and plasma-treated cotton samples. The dyed cotton fabrics were post-treated in a colloidal silver solution [71]. A dyeing bath was prepared with 4% owf Bezathren Blau BCE, 15 ml/l NaOH 38°Bé and 3.5 g/l Na₂S₂O₄. The liquor ratio was 83.3 : 1. The dyeing of cotton fabrics was performed at 60°C for 60 min. The dyed samples were rinsed twice in deionised water for 5 min, post-treated in 2 ml/l HCOOH 85% for 5 min and rinsed in deionised water for 5 min.

2.4. Color measurements

Color measurements of differently modified samples were performed after conditioning them according to the ISO 139 standard. CIE standard illuminant D65/10 was used on a Datacolor Spectraflash SF 600-CT reflection spectrophotometer. The aperture diameter of the measuring port of the spectrophotometer was 9 mm.

2.5. Elemental and antimicrobial analysis

The quantity of adsorbed silver was determined using ICP-MS. This technique combines a high-temperature inductively coupled plasma (ICP) source with a mass spectrometer (MS). The antibacterial efficiency of functionalized textiles was determined using microbiological tests according to the ASTM Designation: E 2149–01 method. Antibacterial activity of the cotton fabrics was tested by a certified laboratory against *Staphylococcus aureus* (ATCC 25923), *Escherichia coli* (ATCC 25922), *Streptococcus faecalis* (ATCC 27853) and *Pseudomonas aeruginosa* (ATCC 27853).

3. Results and discussion

The influence of different plasma systems on the adhesion of nanoparticles is discussed. The emphasis of the study is to use minimal concentrations, initially, of nanoparticles for loading onto textiles and to achieve maximum quantity on the material. Exhaust dyeing process was used for loading of silver nanoparticles onto textiles. Before applying nanoparticles to any material, its surface needs to be adequately prepared and chemically and morphologically well analyzed. Only good conditions on the substrate surface can provide a qualitative deposition of particles [73]. In literature one can find quotations of XPS analysis of plasma modified cotton substrates which were pre-prepared with various procedures prior to plasma modification (i.e. alkaline boiling, scouring, laundering). But to study plasma modification of cotton it is important to know about the surface changes of substrates that were not cleaned or otherwise pre-prepared. Therefore, the chemical surface changes were evaluated for raw, bleached and bleached/mercerized cotton before and after plasma treatment.

The surface of raw untreated cotton fabric contains a high concentration of carbon and a low concentration of oxygen. This is not characteristic for native cellulose [74]. XPS spectrum C 1s of cellulose also does not include C-C/C-H bonds (Figure 3). The surface of raw
cotton is rich in C atoms (C-C/C-H bonds), what could indicate the presence of C-C/ C-H bond rich substances, such as waxes, pectin and proteins. The surfaces of bleached and bleached/mercerized cotton fabrics are alike but very different from raw cotton. Bleached and bleached/mercerized cotton samples are pre-oxidized due to the scouring, bleaching and mercerizing process, and therefore more similar to native cellulose. After modifications with atmospheric air corona plasma and water vapor low-pressure plasma cotton samples contain a higher O/C ratio (the samples contain more of the oxygen and less of the carbon atoms) (Figure 4).

**Figure 3.** Relative concentration of carbon bonds on the surface of cotton samples: R – raw cotton, B – bleached cotton, BM – bleached/mercerized cotton, AP – atmospheric plasma treatment, LP – low-pressure plasma treatment

**Figure 4.** The concentration ratio between oxygen and carbon on the surface of cotton samples: R – raw cotton, B – bleached cotton, BM – bleached/mercerized cotton, AP – atmospheric plasma treatment, LP – low-pressure plasma treatment
The increase of O/C ratio is expected since plasma interaction with cotton causes the surface oxidation. Changes of C-atom bonds on raw cotton samples after corona and low-pressure plasma treatment are visible in Figure 3 as the ratio of C-O and C=O bonds increased. The results show that increase of relative concentration of C-O bonds is distinctive after corona plasma treatment (41 %) than after low-pressure plasma treatment (23.9 %). It is similar for C=O bonds. The relative concentration of C=O bonds on the surface of raw cotton increases to 16.6 % after corona plasma treatment and to 8.2 % after low-pressure plasma treatment. Both plasma treatments result in a formation of O-C=O bonds. C 1s spectrum of plasma-treated samples resembles to the spectra of native cellulose, which could indicate that plasma selectively removed the noncellulosic parts present on a surface of a raw untreated cotton fabric. After plasma treatment the oxygen content on surface of bleached and bleached/mercerized cotton samples increases. After a treatment with corona plasma the content of oxygen on bleached cotton sample increases from 34.3 at% to 44.5 at%, while the treatment with low-pressure plasma increases oxygen to 36.8 at%. After both plasma treatments the content of C-O remains the same (~55 %), the content of C=O bonds increases and appearance of O-C=O bonds is noticeable. Increase of bonds is distinctive after corona plasma treatment than after low-pressure plasma treatment. Content of C-C/C-H bonds decreases after both plasma treatments. Increase of O/C ratio on plasma-treated bleached/mercerized cotton samples is distinctive after corona plasma treatment, where the oxygen concentration increases to 45.3 at%, while increses to 37.5 at% after low-pressure plasma treatment. Due to oxidation process in plasma, the content of C-C/C-H bonds deceases and the change is more noticeable for bleached/mercerized cotton than for a bleached cotton fabric. For bleached/mercerized cotton sample concentration of C-O bonds is increased in the case of corona plasma treatment, from 47.6 % to 69.3 %, while it remains almost equal after low-pressure plasma treatment (47.8 %). After both plasma treatments the content of C=O bonds increases and appearance of O-C=O bonds is noticeable. These changes are more distinct after low-pressure plasma treatment (20.7 % and 6.8 %) than after corona plasma treatment (15.5 % and 3.9 %). The results summarized in Figure 4 show higher concentration of oxygen on atmospheric air corona and water vapor low-pressure plasma-treated raw cotton than on untreated bleached or bleached/mercerized cotton. From these results it can be concluded that by using plasma technology some of the technological processes of pretreatment of cotton fabrics before dyeing can be avoided. Plasma-treated raw cotton fabric absorbs the same or more of dyestuff as untreated bleached or bleached/mercerized cotton fabric [3, 65, 65, 76]. Reactive dyes are typical anionic dyes containing reactive systems which in alkaline media make bonds with –OH groups of cotton fibers. Increase of dyeability of cotton treated with atmospheric air corona plasma or water vapor low-pressure plasma is correlated to an increase of the number of hydrophilic groups on the surface of the fibers. In Figure 5 the correlation between color differences (expressed as ΔE*) of reactive dyed cotton and differences in O/C ratio (expressed as ΔO/C) of untreated and plasma-treated cotton is presented. The most perceptible changes in color differences (ΔE*) are noticeable when differences in O/C ratio (ΔO/C) are higher. Visible color differences between untreated and water vapor plasma-treated cotton were noticeable for raw (ΔE* = 2.20) and bleached/mercerized cotton (ΔE* = 1.07).
Figure 5. The correlation between color differences (expressed as $\Delta E^*$) of reactive dyed cotton and differences in O/C ratio (expressed as $\Delta O/C$) of untreated and plasma-treated cotton (R – raw cotton, B – bleached cotton, BM – bleached/mercerized cotton).

Figure 6. The concentration ratio between oxygen and carbon on the surface of untreated (BM) and CF$_4$ plasma-treated (BM_CF4) cotton samples.

Figure 7. Relative concentration of carbon bonds on the surface of untreated (BM) and CF$_4$ plasma-treated (BM_CF4) cotton samples.
The samples modified in tetrafluoromethane low-pressure plasma (CF\textsubscript{4} plasma) gave different results. There was no visible color difference between untreated and CF\textsubscript{4} plasma-treated bleached/mercerized cotton samples ($\Delta E^* = 0.62$). Both samples were practically equally colored. Treating cotton fabrics for 10 sec with CF\textsubscript{4} plasma does not influence their dyeing properties. The results of XPS study show a small increase in the concentration of oxygen after CF\textsubscript{4} plasma treatment, but the result is hardly remarkable (Figure 6 and 7).

**Figure 8.** SEM images of untreated and plasma-treated cotton samples

It is interesting, however, that no fluorine was observed in the XPS spectra, but that the additional ISE analysis indicated the presence of $<5$ ppm of total fluoride on CF\textsubscript{4} plasma-treated
samples. Here, it is worth mentioning that we are not the first group to observe little or no fluorine on organic materials treated with CF₄ plasma [76, 77]. Although XPS analysis did not show specific chemical surface differences between untreated and CF₄ plasma-treated cotton samples, the SEM analysis showed strongly modified surface morphology of plasma-treated cotton (Figure 8), while smaller changes of the surface morphology of cotton samples treated with atmospheric air corona plasma and water vapor low-pressure plasma are noticed.

SEM image of untreated cotton (Figure 8 a) shows a typical grooved surface morphology with macrofibrils oriented predominantly in the direction of the fiber axis. The outlines of the macrofibrils are still visible, and they are smooth and distinct due to the presence of an amorphous layer covering the fiber. The surface of corona plasma-treated cotton has striped, cleaned and more distinct macrofibrilar structure (Figure 8 b). The same effect can be noticeable on the surface of cotton fibers treated with water vapor low-pressure plasma (Figure 8 c). The plasma-treated fiber surface remains grooved and the macrofibrile structure has gained a much sharper outline. The individual macrofibrils (0.2–1 nm) and their transversal connections are visible in the primary cell wall. Between them, narrow voids thinner than 10 nm are noticeable. The surface morphology of CF₄ plasma-treated cotton (Figure 8 d) is very different comparing to those treated with water vapor low-pressure or corona plasma. CF₄ plasma-treated cotton has an extremely rough and nanostructured surface with dimensions of the grains roughly between 150 and 500 nm. Dissociation energies of plasma molecules are the reason for such rich etched surface. Both CF₄ and H₂O molecules get dissociated in our plasma [78]. The dissociation energy of CF₄ is 12.6 eV [79] while the ionization energy of CF₄ is about 16 eV, which is much higher than the dissociation energy of water vapor or OH molecules, which is at about 5 and 4 eV, respectively. The electrons with energy of few eV are therefore likely to dissociate water and OH molecules rather than dissociate the CF₄ molecules. The result is an extremely high dissociation fraction of water molecules and a moderate dissociation fraction of CF₄ molecules. Since the partial pressures of water and CF₄ are comparable, it can be concluded that the density of O and OH radicals in our plasma is at least as high as the density of CF₄ radicals if not more so. The textile sample exposed to plasma is therefore subjected to interact with CF₄, O, OH, F and H radicals. The density of H is probably as high as that of F so extensive recombination to HF is expected. CF₄ radicals tend to graft onto the textile, but the grafting probability on cellulose is low compared to the interaction probability with O and OH radicals. O and OH radicals are extremely reactive and cause etching of cellulose. Fluorine atoms are efficient at abstracting hydrogen in the first step of the oxidation reaction. In addition, the presence of fluorine atoms in the plasma enhances the dissociation of the oxygen, further increasing the ashing rates [80]. CF₄ is the gas most commonly added to oxygen to enhance the generation of atomic oxygen in plasma and to increase polymer etch rates [81].

While the surface of plasma-treated cotton was changed, the mechanical properties of cotton fabrics did not alter after plasma modification. The breaking strength and elongation of textiles practically do not change (Figure 9 and 10) [3, 27]. These results are in accordance with the results obtained by other authors [82-85]. Plasma modification of textiles does not impair their mechanical properties.
A textile surface with such extremely rich surface morphology (as seen from SEM) is likely to influence higher adsorption of silver nanoparticles, which is in accordance with our ICP-MS results in Table 1, where the quantity of adsorbed silver onto cotton samples is presented.

From the results summarized in Table 1, it is clear that 30 nm silver nanoparticles are more adhesive to the cotton fabric than 80 nm silver nanoparticles. Regarding their volume, nanoparticles have a high specific surface area. By decreasing the size of a particle, its surface distribution rate increases [87]. The quantity of adsorbed silver on untreated bleached/mercerized cotton was 32 ppm when 30 nm silver nanoparticles were used and 13 ppm when 80 nm silver nanoparticles were used. Similar trend can be observed when cotton was modified with plasma. When cotton was treated with water vapor low-pressure plasma the quantity of adsorbed 30 nm silver nanoparticles was 50 ppm and the quantity of adsorbed 80 nm silver nanoparticles was 17 ppm, which means that adsorption of 80 nm silver nanoparticles was three times lower than the adsorption of 30 nm silver nanoparticles. The results show that plasma heavily modifies the morphology and surface chemical properties of cotton.
cotton and by that has a great impact on the adsorption of silver nanoparticles onto fabrics. Atmospheric air corona treatment of cotton fabrics enhanced the quantity of silver onto raw cotton up to 4 times and onto bleached/mercerized cotton up to 2 times [64]. The adsorption of 80 nm silver nanoparticles onto CF₄ plasma-treated cotton was 2 times higher and onto water vapor plasma-treated cotton was 1.3 times higher than on untreated cotton. These fabrics had a sufficient antimicrobial effectiveness against *Escherichia coli* and *Pseudomonas aeruginosa* (Table 1) [3]. The adsorption of 30 nm silver nanoparticles onto CF₄ plasma-treated cotton is 1.7 times higher and onto water vapor plasma-treated cotton was 1.6 times higher than on untreated cotton. This gave a good antimicrobial effectiveness against *Enterococcus faecalis* and *Pseudomonas aeruginosa* (Table 1) [27].

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<th>Plasma modification of cotton</th>
<th>Functionalization with silver nanoparticles</th>
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<tr>
<td>Corona air</td>
<td>80 nm</td>
<td>39</td>
<td>–a</td>
</tr>
<tr>
<td>ICRF water vapor</td>
<td>30 nm</td>
<td>50</td>
<td>52 (<em>E. coli</em>)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>64 (<em>P. aeruginosa</em>)</td>
</tr>
<tr>
<td></td>
<td>80 nm</td>
<td>17</td>
<td>–a</td>
</tr>
<tr>
<td>ICRF CF₄</td>
<td>30 nm</td>
<td>54</td>
<td>68 (<em>E. faecalis</em>)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>77 (<em>P. aeruginosa</em>)</td>
</tr>
<tr>
<td></td>
<td>80 nm</td>
<td>26</td>
<td>–a</td>
</tr>
</tbody>
</table>

–a no bacterial reduction

Table 1. The quantity of silver (ppm) and antimicrobial efficiency expressed as a bacterial reduction (%) of untreated and plasma-treated cotton samples functionalized with powdered silver nanoparticles

Although the purpose of our research was to study the efficiency and appropriateness of plasma modification of textiles in order to achieve a higher adsorption of nanoparticles onto their surfaces, the wash fastness of functionalized textiles was examined as well. Wash fastness test was carried out in a laboratory apparatus Launder-O-Meter [3, 27]. The samples were washed repetitively ten times at 95°C in a solution of 5 g/l of SDC standard detergent and 2 g/l of Na₂CO₃ (where 10 globules were added). The duration of the washing cycles was 30 min. After every wash cycle, the samples were rinsed twice in distilled water and then for 10 minutes under a tap water, which was followed by squeezing and air drying. In Table 2 the results of silver quantity on washed cotton samples are presented. From the results it can be seen that after ten times washing at 95°C the quantity of silver on the cotton samples decreased (Table 2).
Plasma modification of cotton
Functionalization with silver nanoparticles

<table>
<thead>
<tr>
<th>Plasma modification of cotton</th>
<th>Functionalization with silver nanoparticles</th>
<th>Ag quantity (ppm) on cotton before washing</th>
<th>Ag quantity (ppm) on cotton after washing</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICRF water vapor</td>
<td>30 nm</td>
<td>50</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>80 nm</td>
<td>17</td>
<td>10</td>
</tr>
<tr>
<td>ICRF CF₄</td>
<td>30 nm</td>
<td>54</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>80 nm</td>
<td>26</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 2. The quantity of silver (ppm) before and after washing

When cotton was modified by water vapor plasma the quantity of 30 nm silver nanoparticles decreased by 48%, and when modified by CF₄ plasma the quantity of silver nanoparticles decreased by 34%. The drop in the concentration of silver on the cotton after ten wash cycles is also observed with the 80 nm silver nanoparticles. Cotton that is treated with water vapor plasma loses 41%; however, cotton treated with CF₄ plasma loses 15% of the silver nanoparticles. After a 10-second treatment with CF₄ plasma, the surface of the bleached/mercerized cotton is more liable to the adsorption of silver nanoparticles than the surface that was modified by the water vapor plasma. The particle adhesion is a complex phenomenon depending on the interaction mechanism between particles and the surface of a material. Adsorption of silver nanoparticles onto cotton from a dyeing bath is much higher for smaller particles than for larger ones. When particles are already on the surface of cotton fibers the attractive interactions and forces are stronger for 80 nm silver nanoparticles than for 30 nm silver nanoparticles. That is the reason for a better wash durability of 80 nm silver particles. From the results presented in Table 1 and 2, it is evident that the quantity of silver on untreated and unwashed cotton is almost the same as on the samples that were modified by plasma and washed 10 times at 95°C.

The further experiments in functionalization of cotton with other forms of silver nanoparticles (i.e. commercial form RucoBac AGP and laboratory synthesized colloidal silver nanoparticles) were based on the obtained adhesion results of silver nanoparticles of known dimensions. The application of RucoBac AGP and synthesized colloidal silver nanoparticles was carried on a bleached/mercerized cotton fabric modified by atmospheric air corona plasma and water vapor low-pressure plasma.

The exhaustion method was used for the deposition of RucoBac AGP onto blank dyed, dyed, plasma-treated blank dyed and plasma-treated dyed cotton samples. 0.1% of RucoBac AGP was used, which represents a half of the lowest concentration recommended by the agent producer. The reason for such a decision was to verify the possibility in achieving good antibacterial efficiency of a cotton fabric with the use of a very low concentration of silver composite. The liquor ratio was 10 : 1, and the treatment time 30 min at 50°C. Afterwards, the samples were dried at 130°C for 4 min. The results of the ICP-MS and antimicrobial analysis of samples are presented in Table 3.
The results summarized in Table 3 show low adsorption of silver onto untreated blank dyed cotton. The adsorption of silver onto corona modified cotton did not significantly increase. Both samples do not exhibit the antimicrobial effectiveness. However, treating cotton with water vapor low-pressure plasma increased the adsorption of silver onto cotton up to 7 times, which resulted in an excellent antimicrobial effectiveness against *Streptococcus faecalis* and a sufficient antimicrobial effectiveness against *Escherichia coli*. The adsorption of silver significantly increased when RucoBac AGP was applied onto dyed cotton fabric, regardless of plasma treatment. RucoBac AGP is a nano-dispersion of TiO$_2$ as the carrier of the active component AgCl. In the presence of moisture, silver cations react with hydroxyl functional cellulosic groups and are attached to each other electrostatically. The presence of a reactive dye on cotton and the introduction of additional covalently bound sulfonic acid groups will facilitate the uptake of a cationic antimicrobial agent [87]. Therefore, it is possible to conclude that RucoBac AGP is bound to the cotton surface through sulfonic groups of a covalently bound dye and through partially ionized hydroxyl and carboxyl groups present on the fiber [72]. The significant increased adsorption of silver can be also noticed with samples modified by water vapor low-pressure plasma and dyeing, while there was no noticeable change when samples were modified by corona plasma. Results obtained from XPS analysis showed that plasma modification of bleached/mercerized cotton increased the content of oxygen on the surface. In addition, after both plasma treatments the appearance of new bonds was noticeable (O-C=O) and the content of C=O bonds increased. That means that oxygen rich functional groups incurred on the surface of plasma modified cotton. These changes were more distinct after low-pressure plasma treatment than after corona plasma:

<table>
<thead>
<tr>
<th>Sample Treatment</th>
<th>Plasma treatment of cotton</th>
<th>Ag quantity (ppm) on cotton</th>
<th>Bacterial reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functionalization with 0.1 % RucoBac AGP</td>
<td>Untreated</td>
<td>1.5</td>
<td>—$^a$</td>
</tr>
<tr>
<td>Corona air</td>
<td>1.8</td>
<td>—$^a$</td>
<td></td>
</tr>
<tr>
<td>ICRF water vapor</td>
<td>11</td>
<td>58 (<em>E.coli</em>) 98 (<em>S.faecalis</em>)</td>
<td></td>
</tr>
<tr>
<td>Dyeing with reactive dye and functionalization with 0.1 % RucoBac AGP</td>
<td>Untreated</td>
<td>8.9</td>
<td>100 (<em>E.coli, S.aureus, S.faecalis and P.aeruginosa</em>)</td>
</tr>
<tr>
<td>Corona air</td>
<td>8.4</td>
<td>100 (<em>E.coli, S.aureus, S.faecalis and P.aeruginosa</em>)</td>
<td></td>
</tr>
<tr>
<td>ICRF water vapor</td>
<td>13</td>
<td>80 (<em>S.aureus and E.coli</em>) 100 (<em>S.faecalis</em>)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ no bacterial reduction

Table 3. The quantity of silver (ppm) and antimicrobial efficiency, expressed as a bacterial reduction (%), of untreated and plasma-treated cotton samples functionalized with RucoBac AGP
treatment. The difference in both plasma treatments is noticeable from the ICP-MS results also (Table 3), since the adsorption of RucoBac AGP onto cotton was greater after modification by water vapor low-pressure plasma. Nevertheless, all modified cotton fabrics had an excellent antimicrobial effectiveness against *Staphylococcus aureus*, *Escherichia coli*, *Streptococcus faecalis* and *Pseudomonas aeruginosa*.

The objectives for textile industry have been continuous on-line treatments of fabrics. Low-pressure plasma reactors, such as radio frequency powered plasma, provide greater stability and uniformity but generally require more handling of textile materials through the vacuum system than corona discharges at atmospheric pressures. In this respect, the use of corona plasma is more appropriate for the industry. In our following research when laboratory colloidal silver was used, we focused on treating cotton fabric with atmospheric corona plasma. The synthesis of colloidal silver was performed by reducing silver salt in an aqueous solution at room temperature under argon atmosphere. The procedure was described previously, in section 3.2.1. A synthesis of colloidal silver and loading of silver onto cotton fabric was performed as the second phase after dyeing cotton fabrics with a blue vat dye. To verify whether vat-dyeing influences the adsorption of colloidal silver onto cotton fabric, a blank vat-dyeing procedure (dyeing with all chemicals and no dye) was also performed [71].

Apart from indigo, the vat dyes used in dyeing applications are mainly derivatives of anthraquinone and of higher condensed aromatic ring systems with a closed system of conjugated double bonds. They generally contain two, four or six reducible carbonyl groups [88].

![Figure 11. Scheme of reduction and oxidation process of carbonyl group of vat dye](image)

The vat dyes are insoluble in the keto form (Figure 11a). For dyeing they must be transformed to a water soluble enolate (leuko) form (Figure 11c) by a reduction. This form of the dye is appropriate for cellulose dyeing, but the addition of electrolyte is also required. After the dyeing, the dye in amorphous regions is transformed through leuko acid (Figure 11b) into its original water insoluble form by rinsing and oxidation [89]. The vat dyeing of bleached/mercerized cotton fabric before colloidal silver treatment significantly influences the adsorption of silver onto cotton fabrics [71]. Also the adsorption of silver is influenced by an immersion time of cotton into colloidal silver solution. Although it was proven that modification of cotton by corona plasma strongly influences the adsorption of powdered silver nanoparticles by increasing their quantity on the modified cotton, the experiment using synthetized colloidal silver on corona treated cotton had to be conducted. The Table 4 presents the results of ICP-MS and antimicrobial analysis of untreated, corona and vat dyed colloidal silver loaded cotton.
The results summarized in Table 4 show that atmospheric air corona treatment enhanced the quantity of silver onto dyed cotton up to 1.8 times comparing to the untreated dyed cotton. In addition to the morphological changes induced by plasma (seen by SEM), XPS analysis showed the increase of C-O and C=O bonds and formation of O-C=O bonds on the surface of treated cotton. The increased concentration of oxygen and newly formed bonds contributed to a better adhesion of Ag\(^+\) ions from the colloidal solution onto cellulosic fibers. In addition to the increased number of functional groups containing oxygen, the dyed cotton fabric contains additional anionic sites due to the partial ionization of the molecules of insoluble vat dye. Colloidal silver is produced in a water solution using AgNO\(_3\) reduced by NaBH\(_4\). NaBH\(_4\) also slightly reduces the water insoluble vat dye on the dyed fabric into a slightly soluble form. Although NaBH\(_4\) is not a sufficiently strong reducing agent for dyeing cotton with a vat dye [90], it is nevertheless strong enough to enhance the negative charge of the dye on the fabric [91] such that silver ions (Ag\(^+\)) from a silver colloidal solution can be electrostatically attracted to the dyed cotton surface. It was reported that while Ag\(^+\) ions from a colloidal silver solution are exhausted to the anionic cotton fibers to a high degree because of the attractive electrostatic interactions, the high increase of the adsorption ability of silver nanoparticles caused by the van der Walls forces resulted from the high surface area to volume ratio of these particles [43].

The important goal of our research was to use minimal concentrations, initially, of silver nanoparticles for loading onto textiles and to achieve a maximum quantity on the material, and thus to achieve functionalized cotton textile with an excellent antimicrobial efficiency. Since the cotton fabrics already had an excellent antimicrobial efficiency when functionalized with rather low concentration of silver, the decision was made to verify the possibility in achieving good antibacterial efficiency of a cotton fabric with the use of half of the initial

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Ag quantity (ppm) on cotton</th>
<th>Bacterial reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dyed and functionalized with colloidal silver</td>
<td>24</td>
<td>100 (E.coli, S.aureus, S.faecalis and P.aeruginosa)</td>
</tr>
<tr>
<td>Corona plasma-treated, dyed and functionalized with colloidal silver</td>
<td>43</td>
<td>100 (E.coli, S.aureus, S.faecalis and P.aeruginosa)</td>
</tr>
<tr>
<td>Corona plasma-treated and functionalized with a half of concentration of colloidal silver</td>
<td>1.6</td>
<td>(\sim^*)</td>
</tr>
<tr>
<td>Corona plasma-treated, dyed and functionalized with a half of concentration of colloidal silver</td>
<td>4.6</td>
<td>100 (E.coli, S.aureus, S.faecalis and P.aeruginosa)</td>
</tr>
<tr>
<td>(\sim^*) no bacterial reduction</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. The quantity of silver (ppm) and antimicrobial efficiency, expressed as a bacterial reduction (%), of untreated and plasma-treated cotton samples functionalized with synthetized colloidal silver.
concentration of AgNO$_3$ and NaBH$_4$. In this case, the corona plasma modified and undyed cotton contained 1.6 ppm of silver. The quantity of silver was so low that the fabric did not have an antimicrobial efficiency. However, when cotton fabric was modified by corona plasma and then vat dyed the quantity of silver was 4.6 ppm, which gave the fabric an excellent antimicrobial efficiency against *Staphylococcus aureus*, *Escherichia coli*, *Streptococcus faecalis* and *Pseudomonas aeruginosa*. The antimicrobial analysis showed the antimicrobial ineffectiveness of dyed cotton sample, therefore the dye itself did not contribute to the antibacterial efficiency of the functionalized cotton sample.

4. Conclusion

Our research shows that plasma treatment is an effective method to be used in achieving surface changes on the textile material by changing the functional groups on the textile surface and by changing the morphology of the fibers. The results of adsorption of different forms of silver nanoparticles on untreated and plasma-treated surfaces of fabrics confirm the fact that, for nanotechnological processes, the surface of the material has to be properly prepared. The adsorption of metal nanoparticles on textile materials depends on specific chemical and morphological properties of fibers. Plasma modification of cotton had a positive influence on the increased adsorption of silver nanoparticles loaded during exhaust dyeing process. From the bath, which contained a low concentration of silver nanoparticles, we have successfully applied a greater quantity of silver onto plasma modified cotton (up to four times). In some cases using plasma the dyeability of cotton was also improved. We succeeded to create a cotton fabric containing minimal quantity of silver with an excellent antimicrobial efficiency. This is very interesting from the technological point of view since by this method the quantity of silver in wastewater can be dramatically reduced. Another important result of the research was that plasma modification did not impair the mechanical properties of textiles. By using plasma technology new and improved properties of materials can be created that cannot be achieved by standard procedures, where nanostructuring of natural and synthetic fibers is emphasized. The use of plasma for modification of textiles brings to the textile industry many novelties, since plasma technology can be used as a substitute or as a support to the existing technologies, and by that positively influences the economy and ecology of the industrial processes. The knowledge of using plasma technology enables an introduction of contemporary (state-of-the-art) and ecological process of a textile modification into the textile industry and a development of highly technological products with improved or new properties.

Acknowledgements

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Author details

Marija Gorjanc¹, Marija Gorenšek¹, Petar Jovančić² and Miran Mozetič³

*Address all correspondence to: marija.gorjanc@ntf.uni-lj.si

¹ University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, Ljubljana, Slovenia

² University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia

³ “Jozef Stefan” Institute, Ljubljana, Slovenia

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