Eur. Phys. J. D (2018) 72: 41
https://doi.org/10.1140/epjd/e2017-80680-9

THE EUROPEAN PHYSICAL JOURNAL D

Regular Article

Natural dyeing and UV protection of plasma treated cotton*

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Received 26 October 2017 / Received in final form 19 December 2017
Published online 8 March 2018 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2018

Abstract. Raw cotton fabrics have been exposed to low-pressure non-equilibrium gaseous plasma to improve the adsorption of natural dyes as well as ultraviolet (UV) protection factor. Plasma created in a glass tube by an electrodeless radiofrequency (RF) discharge was created either in oxygen or ammonia at the pressure of 50 Pa to stimulate formation of oxygen and nitrogen groups, respectively. The type and concentration of functional groups was determined by X-ray photoelectron spectroscopy (XPS) and morphological modifications by scanning electron microscopy (SEM). The colour yield for curcumin dye was improved significantly for samples treated with ammonia plasma what was explained by bonding of the dye to surface of amino groups. Contrary, the yield decreased when oxygen plasma treatment was applied due to the negatively charged surface that repels the negatively charged dye molecules. The effect was even more pronounced when using green tea extract as the colouring agent. The colour difference between the untreated and ammonia plasma treated sample increased linearly with plasma treatment time reaching the factor of 3.5 for treatment time of 300 s. The ultraviolet protection factor (UPF) was over 50 indicating excellent protection due to improved adsorption of the dye on the ammonia plasma treated samples.

1 Introduction

The environmental and health related problems due to the use of synthetic dyes for achieving colourful textiles has led to increased research on re-introduction of natural dyes, which have in comparison to synthetic dyes limitations of use, with the main problem associated to their poor adsorption towards cellulose based textiles (i.e. cotton, rayon, bamboo) [1]. In addition to their dyeing properties, natural dyes also have UV-blocking properties [2]. The textiles which possess protection against UV radiation are of great interest due to the increased UV-induced skin problems (allergies, erythema, photoaging, photo-carcinogenesis) [3]. The studies on increasing the adsorption of natural dyes onto cotton were mostly focused on the use of metal mordants (copper, ferrous, potassium, aluminium, etc.), applied before, during or after dyeing with natural dyes [4]. Although the metal mordants create affinity between dye molecule and dyeing substrate, their use is questionable when it comes to the realising the ecological and health aspects of dyeing. With the discharge of such wastewater into the environment, a large amount of metal ions is released that negatively affect the environment. Additionally, by wearing mordanted textiles, the metal ions can be adsorbed by skin, which poses a health risk. Therefore, it is necessary to strive to use environmentally friendly methods of textile processing to increase the adsorption of natural dyes. Alternatives to metal mordants have been proposed, such as use of chitosan or tannin [5,6]. There has been also reported use of plasma, but as a pre-treatment of for chitosan or mordant application before dyeing with natural dye [7,8], or as a method for coating the fibres with copper (plasma sputtering) [9]. It is interesting that so far, the use of solely plasma modification of cellulose fibres for natural dyeing was not yet reported. The purpose of our research was to establish the possibility of using only plasma, as an ecological benign process, for modification of cotton for increased adsorption of natural dyes. In the first part of the research, an influence of plasma-forming gas on modification of cotton and adsorption of curcumin was studied. The curcumin was chosen as a model natural dye, since it is used for dyeing of variety of textiles, but predominantly wool and silk [10]. The second part of the research was focused to increase the adsorption of green tea extract onto cotton in order to improve the protective properties of cotton towards UV-radiation. It was reported that green tea has an active phenolic moiety called "catechin" in its extracted components, which exerts an UV protective property [11]. The plasma-forming gases were chosen according to the knowledge in synthetic and natural dyeing of cotton. It was found that plasma that functionalises the surface of cotton with oxygen rich functional groups increases the adsorption of synthetic dyes onto cotton [12]. On the other hand, natural dyes that include hydroxyl groups in their structure (i.e. curcuma, green tea) adsorb better on substrates

* Contribution to the Topical Issue "Advances in Plasma Chemistry", edited by Slobodan Milošević, Nikša Krstulović, and Holger Kersten.

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Table 1. Criteria and evaluation of UV protection effectiveness of textiles according to AS/NZ standard.

Protection category	UPF value	UV radiation blocked (%)	UPF rating
Good	15–24	93.3–95.8	15, 20
Very good	25–39	95.9–97.4	25, 30, 35
Excellent	40–50, 50 and more	More than 97.5	40, 45, 50, 50+

that include amino functional groups [4]. The latter are not present in cellulose fibres, but are present in wool and silk. However, it was found that amino functional groups can be introduced to cellulose materials by using ammonia plasma [13].

2 Experimental

2.1 Material

Raw 100% cotton fabric (Tekstina d.d., Ajdovščina, Slovenia) was used in this study.

2.2 Surface modification by plasma

Cotton samples were treated in radiofrequency (RF) low-pressure inductively coupled (IC) plasma system. The plasma reactor was composed of 80 cm long borosilicate cylindrical tube with an inner diameter of 3.6 cm. The water cooled copper coil was mounted onto plasma reactor. The plasma reactor was pumped on one side with a two-stage rotary pump, while oxygen (O_2) or ammonia gas (NH_3) was leaked (70 sccm) on the other side of the reactor during treatment of cotton. The constant pressure of gases was established (50 Pa). The power of RF generator which operates at the standard industrial frequency of 13.56 MHz was 100 W. The cotton samples were treated with O_2 plasma for 10 and 30 s, and with NH_3 plasma from 1 to 300 s.

2.3 Optical emission spectroscopy

Plasma was monitored with an optical emission spectroscopy (OES), which is a non-invasive technique. Avantes AvaSpec-3648 Fiber Optic Spectrometer, with a resolution of 0.5 nm in the range from 200 to 1100 nm, was used. The collimating lens was mounted approximately 2 cm from the discharge tube at the centre of the excitation coil and connected to spectrometer via optical fibre. The integration time was rather long, either 5 or 10 s, while IC plasma at low powers is not that bright.

2.4 Extraction of dye and dyeing

The natural dyes of curcumin (Natural Yellow 3) and green tea were extracted in distilled water (100 ml) using 2 g of powdered curcuma rhizome or crushed green tea leaves at 95 °C for 1 h. The mixtures were filtered in order to separate the particles from the extract. The prepared extract was used as a dyebath. Dyeing of untreated and plasma-treated cotton samples was performed by exhaustion method, in laboratory apparatus Lauder-Ometer® (SDL Atlas), at liquor to goods ratio 50:1, at temperature of 90 °C and for 30 min. After dyeing, the samples were washed with distilled water and air dried.

2.5 Surface analysis

The surfaces of untreated and plasma-treated cotton fabrics were analysed for their chemical and morphological properties. The changes in chemical surface composition of cotton after plasma treatment were analysed using X-ray photoelectron spectroscopy (XPS) (Physical Electronics Inc.) [14], and the morphological changes were analysed using scanning electron microscopy (SEM) (JEOL, Japan) [14].

2.6 Measuring the colour

The colour of dyed cotton samples was measured using reflectance spectrophotometer Spectraflash 600 Plus-CT (Datacolor, Switzerland). The CIE $L^*a^*b^*$ colour coordinates and K/S values were determined for untreated and plasma-treated dyed cotton fabrics. The colour difference (ΔE^*) between the untreated and plasma-treated samples dyed with green tea extract was calculated according to equation (1). The colour yield (K/S values) was calculated from reflectance measurements, according to equation (2). All samples were exposed to standard conditions according to ISO 139 prior to performing the measurements.

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}, \tag{1}$$

where ΔL^* is a difference in lightness component, Δa^* is a difference in red-green component and Δb^* is a difference in blue-yellow component.

$$\frac{K}{S} = \frac{(1-R)^2}{2R}, \tag{2}$$

where K is an absorption coefficient, S is a scattering coefficient and R is a reflectance factor.

2.7 Protection against UV radiation

The protection against UV radiation provided by dyed cotton samples was determined by measuring the UV transmittance of fabrics on a Varian Cary 1E UV/Vis spectrophotometer containing a DRA-CA-301 integration sphere and calculating the UV protection factor (UPF) with SolarScreen software. The measurements and calculations were performed in accordance with the AATCC TM 183 standard. The evaluation of UV protection effectiveness of samples was determined according to Australia/New Zealand (AS/NZ) standard criteria (Tab. 1).

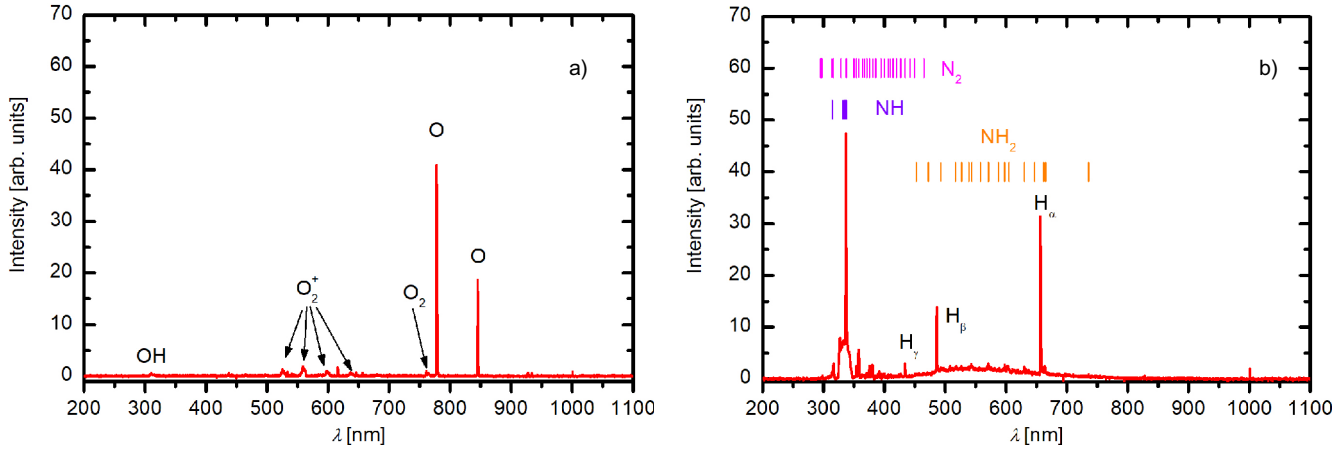

Fig. 1. OES spectra of oxygen IC plasma (a) and ammonia IC plasma (b) during cotton sample treatment. Integration times were 5 and 10 s for oxygen and ammonia plasma, respectively.

3 Results and discussion

The OES spectra of oxygen and ammonia plasma during cotton sample treatment are presented in Figure 1. The most prominent spectral feature in oxygen plasma are oxygen atoms. The excited oxygen molecules and ions are also present, as well as OH radical, which indicates the presence of water vapour. The spectral features in ammonia plasma are: NH_2, NH, N_2 and H atom Balmer lines. At the conditions used in this study, etching products were not observed in OES spectra, because the pumping speed was too high and the power was too low.

The adsorption of natural dyes onto plasma treated cotton was analysed with conventional natural dye curcumin, usually used for dyeing of silk and wool, and unconventional natural dye extracted form green tea. The chemical and morphological changes on the surface of cotton fibres after plasma modifications were analysed with XPS and SEM. From the XPS survey spectra, the surface composition was calculated and the results are presented in Table 2. The untreated raw cotton fibres contain high concentration of carbon (83.7 at%) and low concentration of oxygen (16.3 at%). The surface composition of cellulose, which is the main component of cotton fibres is 54.4 at% carbon and 45.5 at% oxygen [15]. The reason for such high concentration of carbon on our sample of raw cotton is in the noncellulosic components on the surface of fibres, such as waxes, starch, pigments and others. Treating raw cotton with O_2 plasma lowers the concentration of carbon and increases the concentration of oxygen. For a raw cotton treated with O_2 plasma for 30 s, the concentration of carbon is 58.2 at% and concentration of oxygen 41.8 at%. The traditional wet-chemical treatment of raw cotton to prepare it for dyeing with synthetic dyes is performed by souring and bleaching, using large quantities of water, sodium hydroxide and hydrogen peroxide at elevated temperature [16]. The traditional oxidation of raw cotton provides the surface of cotton with 64.9 at% of carbon and 35.1 at% of oxygen. In our case, these values were already reached after modification of raw cotton with O_2 plasma for 10 s. On the surface of raw cotton treated with NH_3 plasma the concentration of carbon also decreases, but not so drastically as in the case of treatment with O_2 plasma. The more important result is an incorporation of nitrogen-rich functional groups on the surface of raw cotton. Longer treatment time with NH_3 plasma increases the concentration of nitrogen on the surface, namely 10 s NH_3 plasma treated sample has the concentration of nitrogen 8.5 at% and 300 s NH_3 plasma treated sample 12.3 at%.

The morphological changes after plasma treatment are presented in Figure 2. Treating raw cotton with O_2 plasma causes the etching of the fibres surface (Fig. 2b). Treating raw cotton with NH_3 plasma does not cause any morphological surface changes, even when treatment time is the highest ($t = 300$ s). This observation is explained by different affinity of the reactive gaseous species towards formation of volatile compounds on the surface of the polymer samples. Oxygen plasma is rich in O-atoms (see Fig. 1a) that readily interact with the cotton materials forming oxocarbon – chemical compounds consisting only of carbon and oxygen [17] as well as low-mass molecular fragments containing C, O and H. The resultant chemical etching is inhomogeneous leading to nanostructuring of originally rather smooth polymer fibres [18]. The affinity of H and NH_x radicals is much lower and so is the etching rate. The radicals created in ammonia plasma (see Fig. 2b) predominantly causes functionalization with N-rich groups upon treatment of polymer materials [19] so etching is regarded a minor effect as long as the specific discharge power is low so that the samples are not heated much.

The first part of the research was to study the influence of plasma-forming gas (O_2 or NH_3) on adsorption of traditional natural dye curcumin onto raw cotton. After dyeing the untreated and plasma-treated cotton samples, the reflectance of the colour on the samples was measured, and colour yield was calculated. The results are presented in Figure 3.

The absorption maximum of all samples is at the wavenumber 450 nm, indicating that plasma did not influence the change in bathochromic or hypochromic shift of absorption spectra of curcumin on the cotton.

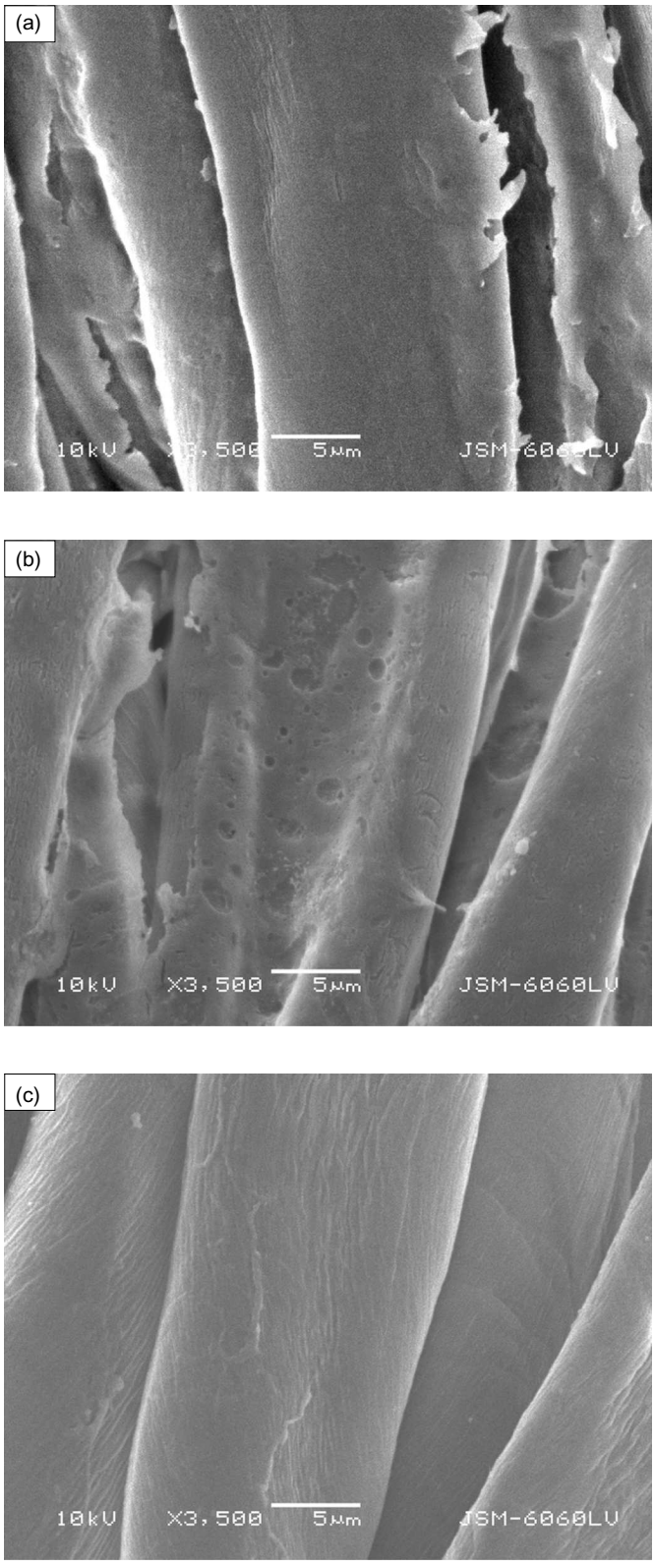

Fig. 2. Scanning electron microscope images of cotton samples: (a) untreated, (b) O_2 plasma treated for 30 s, (c) NH_3 plasma treated for 300 s.

However, from the peak intensity it is clear that the gas selection for plasma generation influences higher or lower adsorption of curcumin towards cotton. The colour yield of untreated cotton is 5.10. As the treatment time with O_2 plasma increases, the colour yield decreases, indicating lower adsorption of curcumin onto cotton. Cotton samples treated with O_2 plasma for 10 and 30 s, have colour yield 4.63 and 3.96, respectively. The opposite effect is noticed on the samples treated with NH_3 plasma. Longer plasma treatment time leads to the increased adsorption of curcumin onto cotton. The sample that was treated with NH_3 plasma for 30 s has a much higher colour yield than untreated sample, with the value of 6.67. The reason for such results is in the chemical changes on the surface of plasma treated cotton (Tab. 2) and not in morphological changes (Fig. 2). Cellulose contains high numbers of –OH functional groups, which give cellulose the negative charge when it is immersed in water. Treating cellulose substrates with oxygen plasma increases the negative potential and therefore increases the repulsion to negatively charged dye molecules [20]. The repulsion between natural dye and cellulose substrates is usually reduced by use of metal salts (i.e. aluminium potassium sulphate, potassium dichromate, stannous chloride, ferrous sulphate and copper sulphate), where the positive metal ions mask the negative potential of cellulose and allow adsorption of natural dye [21]. As presented in our research, the use of toxic metal solutions can be replaced by the use of NH_3 plasma treatment to increase the adsorption of natural dyes onto cotton substrate. From the results it is clear that oxygen-rich surface of cotton decreases the adsorption of curcumin and that adsorption of curcumin is higher on nitrogen-rich surface. These findings lead us to treatment of cotton with NH_3 plasma to increase the adsorption of unconventional dye, extracted from green tea, to achieve very high UPF of cotton. Cotton samples were treated with NH_3 plasma from 1 to 300 s and afterwards dyed with green tea extract. The results of colour difference (ΔE^*) between untreated sample and sample treated with plasma at different treatment time are presented in Figure 4. Higher ΔE^* value between two dyed samples means bigger difference in their colour properties. If the ΔE^* value is higher than 1, it means that the difference is visibly noticeable. The ΔE^* values are lower than 1, when cotton is treated with NH_3 plasma for short time period (i.e. up to 5 s). This means that the concentration of nitrogen-rich groups on the surface of cotton is so low that it does not influence significantly on adsorption of green tea extract. Nevertheless, longer treatment time with NH_3 plasma slowly increases the ΔE^* value between untreated and plasma-treated sample. That way, the highest ΔE^* value ($\Delta E^* = 3.76$) is achieved at the longest plasma treatment time (300 s). The main reason for a such colour difference between untreated and plasma-treated sample is in increased adsorption of green tea extract onto plasma treated cotton. As previously shown in Table 2, longer exposure of cotton to NH_3 plasma increases the concentration of nitrogen-rich groups on the

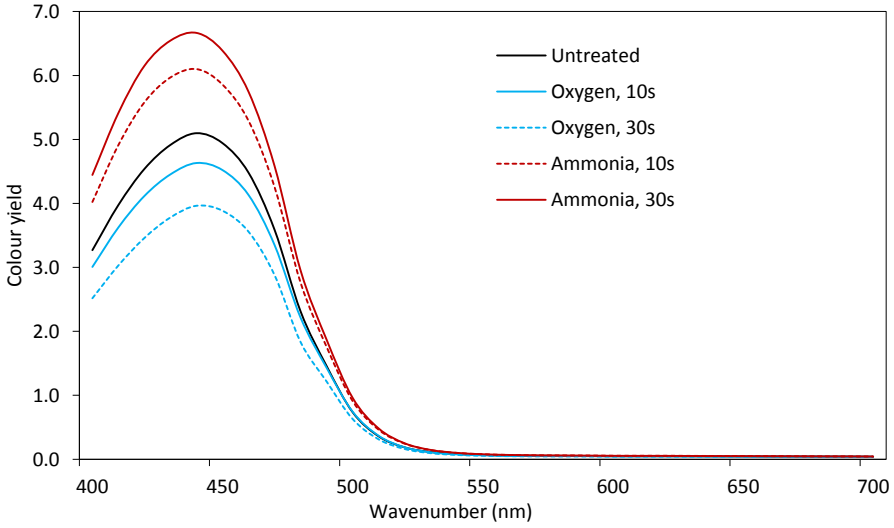

Fig. 3. Colour yield of untreated and plasma-treated cotton dyed with curcumin.

Table 2. The elemental composition (C, O, N) of cotton samples before and after plasma treatment.

Sample	C (at%)	O (at%)	N (at%)
Untreated	83.7	16.3	0
Oxygen, 10 s	64.4	34.7	0
Oxygen, 30 s	58.2	41.8	0
Ammonia, 10 s	61.3	30.2	8.5
Ammonia, 30 s	65.7	22.7	10.4
Ammonia, 300 s	56.9	30.8	12.3

surface of cotton, which positively influence the adsorption of natural dye onto cotton.

In Table 3, the results of UV–Vis spectroscopy for dyed cotton samples are presented.

Increased adsorption of natural dye also influences higher protective properties of cotton towards UV radiation. The results of colour measurements (Fig. 4) are in agreement with UV/Vis results (Tab. 3). The undyed sample has a poor protection against UV radiation, with the UV protection factor (UPF) only 4.12. Dyeing of untreated cotton with green tea extract increases the UPF of cotton to 36.25, which means that such cotton provides a very good protection against UV radiation. This is due to UV-active compound catechin found in green tea extract. Treating cotton with NH_3 plasma for 30 and 300 s increases the UPF to 77.19 and 95.37, respectively. So high values of UPF present the excellent protection against UV radiation, and higher the value, better is the protection. Similar high values were obtained for the metal mordant pre-treated cotton substrates [22]. However, as mentioned earlier the use of metal mordants is not desirable due to their potential toxicity in the environment and during usage of such textiles.

4 Conclusions

An innovative method for pre-treatment of raw cotton fabrics prior to dyeing with a couple of natural dyes was presented. The extracts of curcuma and green tea were used as an ecologically suitable alternative to synthetic dyes currently applied in textile industry. Both dyes are negatively charged in water media so it was expected that the adsorption would be better on the surface of samples treated with plasma suitable for grafting cotton surface with amino groups. Samples were exposed to weakly ionized ammonia plasma. The optical emission spectroscopy confirmed partial dissociation of NH_3 molecules to NH and NH_2 radicals. These radicals interacted slowly with the surface of the cotton fibres causing functionalization with nitrogen-rich groups. XPS analyses revealed monotonic increase of the N content on the polymer surface and the colour difference (ΔE^*) between untreated and plasma treated dyed cotton samples revealed almost linear increase. The plasma treatment did not influence the change in bathochromic or hypochromic shift of absorption spectra of dyed cotton. Furthermore, the surface morphology remained fairly unchanged even after 300 s of treatment with ammonia plasma. The excellent adsorption of the natural dye also allowed for improved protection against harmful ultraviolet radiation. The UV protection factor (UPF) increased significantly even for short treatment times. While it was solely 4 for raw cotton and 36 for dyed cotton without plasma pre-treatment it was as high as 77 already after treatment with ammonia plasma for 30 s and 95 after treatment for 5 min. As a consequence, the UV-R protection rate according to international standards was excellent even for 30 s of

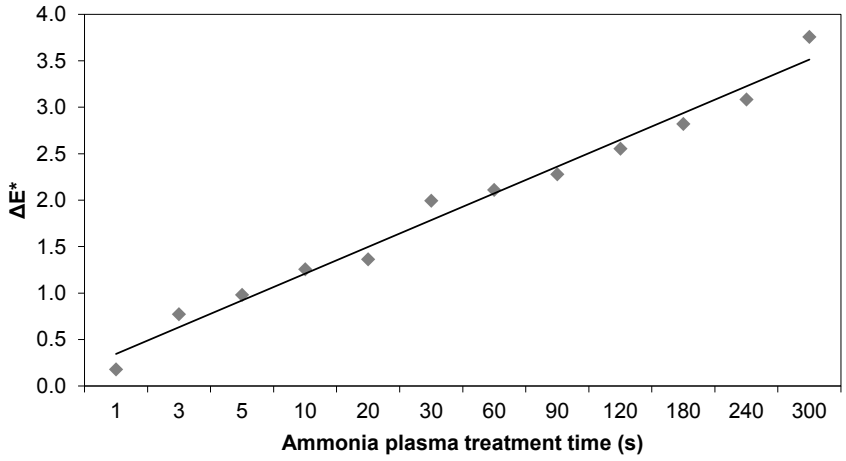

Fig. 4. Colour difference (ΔE^*) between untreated and plasma treated dyed cotton samples.

Table 3. Ultraviolet protection factor (UPF), UPF rating and UV-R protection category of cotton samples dyed with green tea extract.

Sample	UPF	UPF rating	UV-R protection
Undyed	4.12	0	Non-rateable
Untreated	36.25	35	Very good
Ammonia, 30 s	77.19	50+	Excellent
Ammonia, 300 s	95.37	50+	Excellent

plasma treatment. The technology therefore represents a promising substitute to currently employed wet chemical pre-treatment with metal mordants, which represents an ecological hazard.

The financial support from Slovenian Research Agency (P2-0213 and L2-8179) is gratefully acknowledged.

Author contribution statement

M.G. conceived the idea, planned experiments and performed colour, UV/Vis and SEM analysis, and presentation of results. M.M. was involved in planning and supervision of plasma experiments. A.V. performed XPS analysis and presentation of results. R.Z. preformed OES analysis and presentation of results. All authors discussed the results and wrote the manuscript.

References

1. Y. Ding, H.S. Freeman, Color. Technol. **133**, 369 (2017)
2. D. Grifoni, L. Bacci, G. Zipoli, L. Albanese, F. Sabatini, Dyes Pigments **91**, 279 (2011)
3. R.D. Ley, Photobiology **73**, 20 (2001)
4. M. Shahid, S. Islam, F. Mohammad, J. Clean. Prod. **53**, 310 (2013)
5. K. Sin-Hee, Fibers Polym. **7**, 255 (2006)
6. Y.C. Chao, T.H. Ho, Z.J. Cheng, L.H. Kao, P.S. Tsai, Fibers Polym. **18**, 1523 (2017)
7. O.E. Ismal, E. Ozdogan, L. Yildirim, Color. Technol. **129**, 431 (2013)
8. Y. Park, K. Koo, S. Kim, J. Choe, J. Appl. Polym. Sci. **109**, 160 (2008)
9. M. Ghoranneviss, S. Shahidi, A. Anvari, Z. Motaghi, J. Wiener, I. Slamborova, Prog. Org. Coat. **70**, 388 (2011)
10. P.N. Ravindran, K. Niramal Babu, K. Sivaraman (Eds.), *Turmeric: the genus Curcuma* (Taylor & Francis Group, Boca Raton, 2007)
11. S. Kim, Fibers Polym. **7**, 255 (2006)
12. M. Gorjanc, K. Jazbec, M. Mozetič, M. Kert, Fibers Polym. **15**, 2095 (2014)
13. Z. Peršin, R. Zaplotnik, K.S. Kleinschek, Text. Res. J. **84**, 140 (2014)
14. M. Gorjanc, K. Jazbec, M. Sala, R. Zaplotnik, A. Vesel, M. Mozetic, Cellulose **21**, 3007 (2014)
15. M. Gorjanc, J. Kovač, M. Gorenšek, Tekstilec **7/9**, 194 (2010)
16. N. Špička, P. Forte-Tavčer, Mater. Technol. **47**, 409 (2013)
17. R. West (Ed.), *Oxocarbons* (Academic Press, New York, 1980)
18. A. Vesel, M. Mozetič, J. Phys. D: Appl. Phys. **50**, 293001 (2017)
19. A. Vesel, R. Zaplotnik, G. Primc, L. Xiangyu, K. Xu, K.C. Chen, B. Wei, M. Mozetič, Plasma Chem. Plasma Process. **36**, 835 (2016)
20. C. Preston (Ed.), *The dyeing of cellulosic fibres* (Dyer's Company Publications Trust, London, 1986)
21. S. Ashis Kumar, K. Adwaita, in *Natural dyes*, edited by P.A. Kumbasar (InTech, Rijeka, 2011)
22. M.K. Song, E.Y. Song, J. Kor. Soc. Cloth. Text. **29**, 745 (2005)