EFFECT OF PLASMA AND CATIONIZATION PRE-TREATMENTS ON FASTNESS AND UV PROTECTION OF COTTON DYED WITH MADDER

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ABSTRACT

To achieve good colour depth and fastness of naturally dyed fabrics is necessary to use mordants, usually metallic salts, which are potentially harmful to the environment and human health. In this work, the effect of plasma and cationization pre-treatments on cotton fabrics dyed with natural dye madder extract was investigated as environmentally sustainable alternative processes. Air atmospheric dielectric barrier discharge (DBD) plasma treatment showed a slight improvement in fastness to washing and UV light when samples were dyed at pH 11. On the other side, cationization with poly(diallyldimethylammonium chloride) (PDDA) greatly improved the dye uptake onto cotton, but with poor fastness. Meanwhile, the simultaneous pre-treatment with metallic mordants improved significantly the fastness properties, being the PDDA/Fe pre-treatment, followed by dyeing at pH 5, the process which showed the best results regarding colour strength, fastness to UV light, and UV protection.

Keywords: natural dyes; *Rubia tinctorum L.*; textile; DBD plasma; cationization; UV protection

1. INTRODUCTION

Textile dyeing with natural dyes has continuously aroused attention due to environmental and safety concerns, as they constitute an alternative to potentially harmful synthetic dyes [1]. In addition to the fabric's colour, dyeing with natural dyes can also contribute to increasing the protection from ultraviolet (UV) radiation without the need to add hazardous products [2]. However, regarding the cotton dyeing, low colour strength and poor colour fastness of the natural dyes, namely washing and UV light, are huge drawbacks. These difficulties are overcome to a certain extent by using mordants, such as metallic salts. Metallic mordants are traditionally applied in the dyeing process to increase fibre/dye affinity by forming coordinate bonding interactions between fibres, metallic ions, and dye molecules. Although, the non-fixed metallic complexes which remain in the dyebath can lead to pollution if the wastewater is discharged without the appropriate wastewater treatment [3]. Nonetheless, several other surface modifications have been exploited to improve the colour quality of natural dyes, including plasma treatments [4–6], and cationization using bio or synthetic agents [2], [7–10]. Plasma, as the fourth state of matter, is a partially ionized gas composed of a high concentration of reactive species, such as ions, electrons, neutral, excited molecules, free radicals, and photons, which can create new functional sites on fibres by inducing physical and chemical changes on the uppermost surface layers (10 nm) [4], [11]. Dielectric barrier discharge (DBD) plasma is one of the most appellative plasma technology for the treatment of textile substrates since is non-thermal, eco-friendly, and simple to process. The creation of oxygen-containing groups on the surface of the fibres, such as hydroxyl and carboxyl groups, ensures an effective covalent bond of natural precursors to the substrate without altering the intrinsic properties of the material [12]. Regarding cationization, it consists of the introduction of positively charged dyeing sites on the surface of the cellulose fibres which reduces the electrostatic repulsion with anionic dye, increasing the substantivity [9].

This work aimed at studying the effects of two different pre-treatments, plasma and cationization, on the colour depth, washing and UV light fastness of cotton fabrics dyed with the natural dye madder extract. The pre-treatment with two metallic salts was also performed for comparison and to investigate the combined effects of the different treatments. In addition, the protection against UV radiation properties offered by the natural dyeing under the pre-treatments studied was also evaluated.

2. MATERIALS AND METHODS

Materials

Bleached plain-woven cotton fabric (100%, 140 g m^{-2}, 33 warp cm^{-1}, 30 weft cm^{-1}) was provided by Lameirinho - Indústria Têxtil, S.A. (Guimarães, Portugal); Cationization agent poly(diallyldimethylammonium chloride) (PDDA) was supplied by Sigma-Aldrich (Steinheim, Germany) and sodium hydroxide (NaOH) by Merck Millipore (Darmstadt, Germany); Aluminium-potassium sulfate 12-hydrate ($AlK(SO_4)_2.12H_2O$) was acquired from Panreac Química SLU (Barcelona, Spain) and Iron(II) sulfate heptahydrate ($FeSO_4.7H_2O$) from Merck Millipore (Darmstadt, Germany); Natural dye madder (*Rubia tinctorum L.*) extract was offered by the Institute of Natural Fibres & Medicinal Plants (Poznan, Poland).

Methods

DBD plasma

Cotton fabric was pre-treated with air DBD plasma using a semi-industrial machine (Softal Electronics GmbH/University of Minho patented prototype) at room temperature, atmospheric pressure, and with the plasma discharge being produced at high voltage (10 kV) and low frequency (40 kHz). The fabric was treated with a dosage of 2000 W min m^{-2}. The plasma dosage is defined by the Eq. (1):

$$Plasma\ dosage = \frac{N\ P}{v\ l} \quad (1)$$

where N is the number of passages, P is the power (W), v is the velocity (m min^{-1}), and l is the width (0.5 m).

Cationization

Cotton fabric was cationized by the exhaustion method with 5% (on-weight-fabric, owf) of PDDA and 2.5% (owf) of NaOH (50%) using a liquid ratio of 1:40, at 60 °C for 1 h. The process was carried out in an Ibelus machine equipped with an infrared heating system, with a rotation of 50 rpm and 40 cycles, and a gradient of 3 °C min^{-1}. Afterwards, the samples were squeezed and oven-dried (WTC binder oven) at 40 °C, followed by a curing step at 120 °C for 3 min. Finally, the samples were washed with distilled water and dried.

Mordanting

Untreated, plasma and cationized pre-treated cotton samples were mordanted by the exhausting method with 5% (owf) of $AlK(SO_4)_2.12H_2O$ or $FeSO_4.7H_2O$ using a liquid ratio of 1:40, at 90 °C for 1 h. Then, the samples were washed with distilled water and dried.

Dyeing

Untreated, pre-treated/-mordanted samples were dyed by the exhausting method with 3% (owf) of the natural dye madder extract in acid (pH 5) and basic (pH 11) baths, using a liquid ratio of 1:40, at 90 °C for 1 h. Lastly, the dyed samples were washed with distilled water and dried.

Characterization

Colour evaluation

After the dyeing exhaustion process, the remained dye baths were evaluated using the UV-vis spectrophotometer Shimadzu UV 2600 (Shimadzu, Kyoto, Japan). The colour of the dyed samples was also determined through spectrophotometer analysis using the CIELab system. To determine the CIELab coordinates and the colour strength (K/S), three measurements were made at three different positions on the fabrics. The colour strength (K/S) was calculated from the Kubelka-Munk equation, as in Eq. (2):

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

where K is the absorption coefficient, S is the scattering coefficient, and R is the decimal fraction of the reflectance.

Washing fastness

To evaluate the washing fastness of the dyed fabrics, samples were washed according to the ISO 105-C06 A1S standard. Then, the colour difference (ΔE) was determined using Eq. (3):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{3}$$

where L^* is the lightness, a^* red-green (+ red, - green), and b^* yellow-blue (+ yellow, - blue).

UV light fastness

To evaluate the fastness to UV light, the dyed samples were exposed to UV radiation for 2 and 4 h at 50 °C using the QUV equipment (Q-Lab, Westlake, OH, USA) and the ΔE was determined using Eq. (3).

UV protection factor (UPF)

The ability of a fabric to block UV light is given by its UV protection factor (UPF) value. The UPF measurement was performed using the UV-vis spectrophotometer, in the range of 290-400 nm. For each fabric sample, three measurements were performed, rotating the sample 90º. The UPF value for a flat, tension-free dry fabric is given by Eq. (4) (AS/NZS 4399):

$$UPF = \frac{\sum_{290}^{400} E_\lambda \; S_\lambda \; \Delta_\lambda}{\sum_{290}^{400} E_\lambda \; S_\lambda \; T_\lambda \; \Delta_\lambda} \tag{4}$$

where, $E\lambda$ is the relative erythemal spectral efficacy (W m^{-2} nm^{-1}), $S\lambda$ is the solar spectral irradiance (Melbourne), $\Delta\lambda$ corresponds to the measured wavelength range (nm) and $T\lambda$ is the spectral transmittance of the sample (%).

3. RESULTS AND DISCUSSION

The UV-VIS wavelength ranges of the dye solutions obtained after the dyeing processes at pH 5 and pH 11 are shown in Figure 1. The curves of the solutions at pH 5 showed maximum absorbances at around 420 nm (orange), while at pH 11 were around 510 nm (red). Madder dye solutions change colour from yellow to purple when the pH increases due to the ionization of the phenolic hydroxyl group of the alizarin, which is its main component [13]. It was also found that the exhaustion was higher under acidic conditions (pH 5), as the absorbance is lower. Regarding the effect of the pre-treatments, plasma contributed to greater exhaustion, though the cationization process was much more effective due to the ionic attraction between the protonated amino groups present on the modified cotton fibres with the anionic dye.

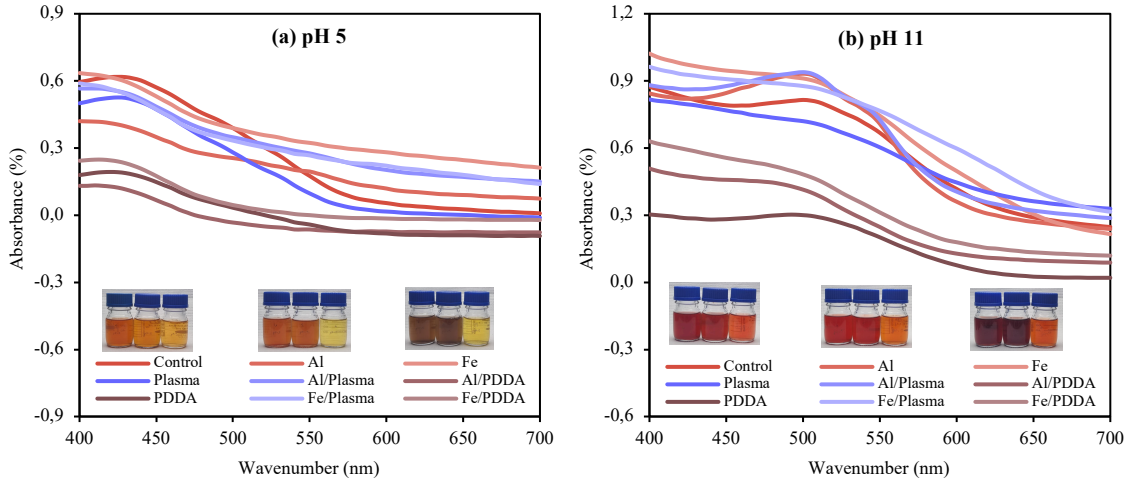

Figure 1. UV-vis spectra of the solutions after the dyeing in acidic and basic conditions, (a) pH 5, and (b) pH 11.

The data presented in Table 1 outlines the CIELab coordinates of the dyed samples as well their photos, and Figure 2 shows the a*-b* colour space position.

Table 1. CIELab coordinates of the samples dyed in acidic and basic conditions.

	pH 5	L	a*	b*	pH 11	L	a*	b*
Control		80.27	9.98	14.67		77.63	18.10	4.56
Plasma		78.75	8.13	14.84		77.31	17.05	6.57
PDDA		62.15	14.19	7.70		56.15	18.11	0.78
Al		66.86	23.88	8.30		77.57	19.87	6.68
Al/Plasma		67.98	19.87	7.07		78.40	17.32	5.50
Al/PDDA		62.89	25.09	9.66		63.30	24.56	7.18
Fe		62.04	4.52	6.00		68.00	7.74	10.77
Fe/Plasma		61.45	4.31	4.86		70.39	7.12	7.02

Fe/PDDA		54.27	6.78	6.61		54.77	8.96	3.39

The pH of the dyeing baths led to a slight difference in the colour shades of the samples, being overall less yellowish and more reddish at pH 11. Furthermore, darker colours were obtained at pH 5 (lower L*) when cotton was pre-treated with metallic salts, whereas without the metallic mordanting darker colours were obtained at pH 11.

About the effect of the pre-treatments is noticeable that the different pre-treatments/mordants led to a difference in the colour shade as well in the lightness. As presented in Figure 2, samples mordanted with iron salt showed the lower a* values (less reddish) and samples mordanted with aluminium salt showed the higher a* values (more reddish). Moreover, darker colours were obtained in the samples pre-treated, indicating an increased fibre/dye interaction.

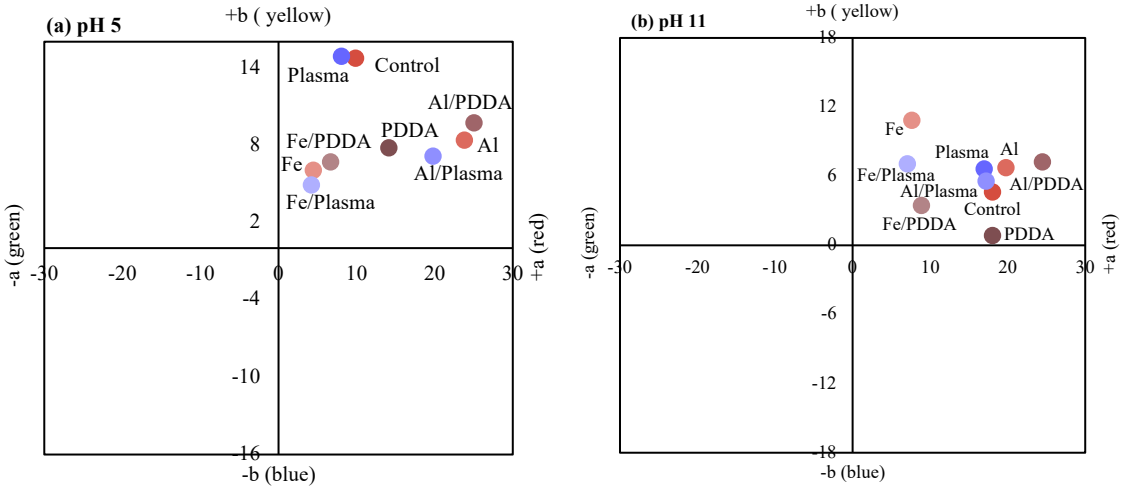

Figure 2. CIELab colour space position of the cotton samples dyed in acidic and basic conditions, (a) pH 5, and (b) pH 11.

As for the colour strength (K/S), Figure 3 (a), in general, higher values were obtained in the samples dyed at pH 5, and in the cationized and mordanted samples, the pH did not influence the obtained K/S values. The control sample showed the lowest K/S as the main component of madder dye, alizarin, which has a low affinity for cotton fabrics and the interaction is mostly via weak van der Waals forces, hydrogen bonding and hydrophobic interactions [14]. Regarding the plasma treatment, there were no differences in colour depth, while cationization led to a significant increase in K/S. After washing with detergent, the colour depth decreased significantly, and the major differences are seen in samples previously cationized. However, concerning the colour fastness to washing, Figure 3 (b), in the samples subsequently mordanted, either with aluminium (Al) or with iron (Fe) salts, the colour difference (ΔE) was much lower. The K/S values obtained after washing for Al/PDDA and Fe/PDDA samples when compared to the Al and Fe samples showed that there was a synergistic effect between the metallic salts and PDDA.

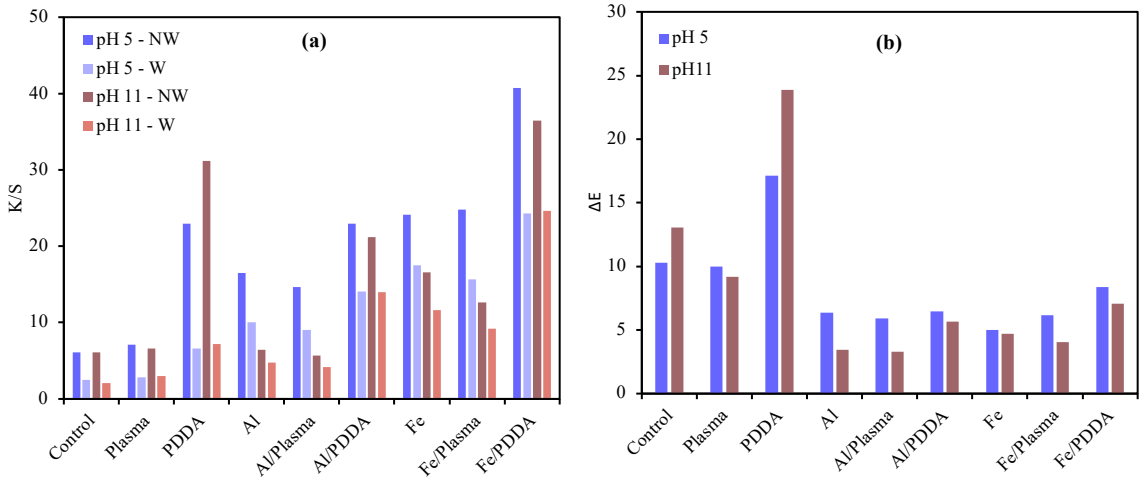

Figure 3. (a) colour strength (K/S) of the dyed samples before (NW) and after washing (W), (b) and colour difference (ΔE) obtained after the washing fastness test.

Concerning the colour fastness to UV radiation exposure, the pre-treatments did not prevent the photofading, however, it is important to note that cationized and mordanted samples presented significantly high K/S values. Moreover, contrary to the expectations, overall, the mordanted samples showed the highest ΔE in the washed samples, being the difference higher in the samples dyed at pH 5.

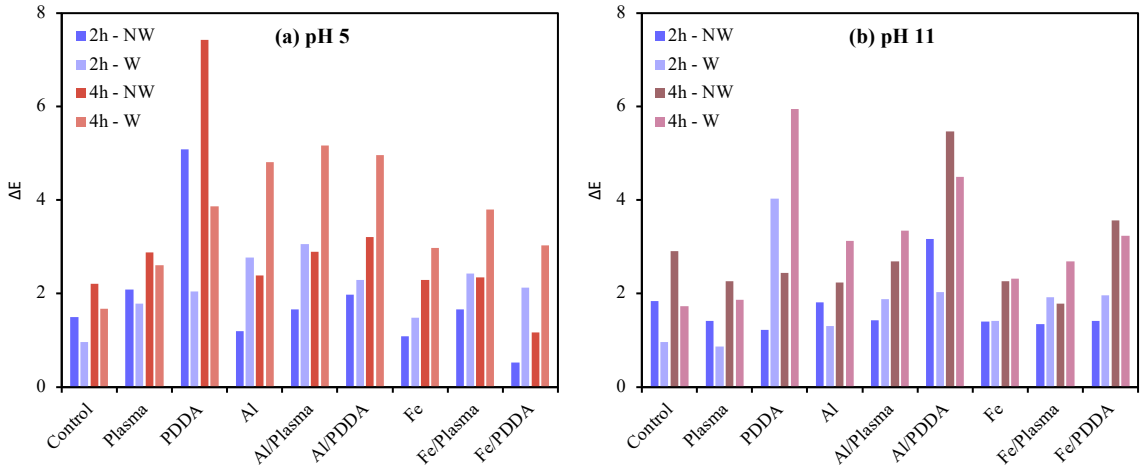

Figure 4. Colour difference (ΔE) obtained for the samples before (NW) and after washing (W) after the exposure to UV light radiation for 2 and 4 h, (a) pH 5, and (b) pH 11.

The UV protection factor (UPF), a measurement used to classify the UV protection of textile materials, obtained for the different dyed samples is presented in Figure 5. The capacity of the dyed fabrics to protect against UV radiation depends on many factors including the uniformity and depth of shade after the dyeing [2]. The UPF was improved after dyeing. Although, the cationization with PDDA and the mordanting processes contributed to obtaining higher UPF, which can be ascribed to the much higher colour depth.

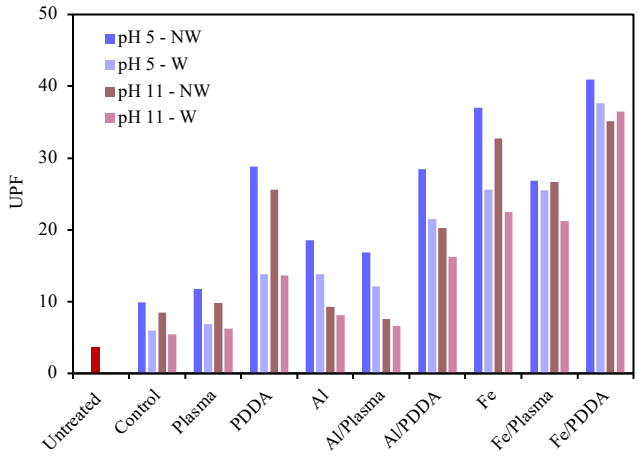

Figure 5. UV protection factor (UPF) of the samples before (NW) and after washing (W).

4. CONCLUSIONS

The role of plasma and cationization pre-treatments on the fastness and UV protection of cotton fabric dyed with the natural dye extract madder has been presented. The results demonstrated that treatment with plasma only contributes to a slight improvement in fastness to washing and UV light when samples were dyed at pH 11. Cationization with PDDA greatly improved the dye uptake onto cotton, thus offering greater UV protection. Nevertheless, the application of metallic mordants was found to be necessary due to the poor fastness of those samples.

5. ACKNOWLEDGMENTS

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