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DYEING OF COTTON WITH MADDER USING (BIO)MORDANTS: EFFECTS ON FASTNESS AND UV PROTECTION PROPERTIES

Cátia Alves¹, Marta Fernandes¹, Rui Rodrigues¹, Andrea Zille^{1(*)}

¹ Centre for Textile Science and Technology (2C2T), Campus de Azurém, Universidade do Minho, 4800-058 Guimarães, Portugal

(*) Email: azille@2c2t.uminho.pt

ABSTRACT

This work aimed at studying the dyeing of cotton fabrics with madder extract using two biomordants, *quebracho* tree extract (*Schinopsis spp.*) and laccase. Pre-treatment with *quebracho* increased the colour strength, washing and UV light fastness, and UV protection, while laccase only shows an increase in the UV light fastness. The application of biomordants together with the metal ones (aluminium or iron salts) led to an improved UV light fastness compared to the samples mordanted only with metal salts. Meanwhile, although the colour strength was lower than in the metal-mordanted samples, greater UV protection factors were obtained in the samples pre-treated with *quebracho* or laccase and iron salt.

KEYWORDS

Natural dyeing, *Rubia tinctorum L.*, metal complex, tannin, laccase.

INTRODUCTION

Textile dyeing contributes severely to environmental pollution, being the natural dyeing an ecological alternative to synthetic dyes. Although, the achievement of good fastness properties is difficult, particularly in cotton due to the poor affinity between the negatively charged fibres and anionic dyes. Therefore, to improve the stability of natural dyes usually are used metal mordants, as they form coordination complexes with the natural dye molecule. Nonetheless, metal salts as mordants pose environmental and human health risks, being the use of biomordants as a nontoxic replacement to overturn those negative issues [1].

Some biomordants such as tannins [1], enzymes [2,3], and biowastes [4] are already being used. Tannins are naturally occurring water soluble polyphenolic compounds of high molecular weight (about 500–3000) containing phenolic hydroxyl groups [5]. *Quebracho* tree extract (*Schinopsis spp.*) is a source of condensed tannins (~20%) [6]. Phenolic hydroxyl groups of tannins enable them to form effective crosslinks with different types of fibres and dyes and help in colour fixation [7]. In the work developed by Phan et al., biomordants consisting of phenolic moieties, gallic acid and tannic acid, improved the light fastness of anthocyanins, as they carry UV-protective/antioxidant properties [1]. This can be ascribed to the formation of a π -complex between the dye and biomordant. Tannins such as tannic acid are often combined with a metal salt to improve the overall fastness of natural dyes [8]. They can fix metallic salts by forming insoluble tannates. These tannates form insoluble lakes with the natural dyes during the dyeing process, improving the fastness properties [5]. Regarding laccase, it consists of multicopper polyphenol enzymes capable of oxidizing phenolic hydroxyl by one-electron oxidation of phenolic to form phenoxy free radicals. Then, the reactive species can also undergo enzymatic oxidation forming o-quinones or polymerizing spontaneously in a non-enzymatic pathway [9]. By catalyzing the



coupling or polymerization of natural dyes containing phenolic hydroxyl groups, laccase can contribute to obtaining deeper colours and enhance the fastness of the dyes [2].

The purpose of this work was to study the natural dyeing of cotton with madder extract considering the use of biomordants to increase the colour strength, fastness and impart UV protection properties. For this, cotton fabric was pre-mordanted with *quebracho* or laccase, and in mixtures with a small amount of aluminium or iron salts.

MATERIALS AND METHODS

Materials

Bleached plain woven cotton fabric (100%, 140 g m⁻², 33 warp cm⁻¹, 30 weft cm⁻¹) was obtained from Lameirinho - Indústria Têxtil, S.A. (Guimarães, Portugal); Aluminium-potassium sulfate 12-hydrate (AlK(SO₄)₂·12H₂O) was acquired from Panreac Química SLU (Barcelona, Spain) and Iron(II) sulfate heptahydrate (FeSO₄·7H₂O) from Merck Millipore (Darmstadt, Germany); *Quebracho* tree extract (*Schinopsis spp.*) was supplied by Sanderma (Alcanena, Portugal) and Laccase by Novozymes (Bagsvaerd, Denmark); Natural dye madder (*Rubia tinctorum L.*) extract was offered by the Institute of Natural Fibres & Medicinal Plants (Poznan, Poland).

Methods

Pre-treatment - cotton samples were mordanted by the exhaustion method with 5% (on-weight-fabric, owf) of *quebracho* or laccase (2000 U mL⁻¹) and in mixtures with 0.1% (owf) of AlK(SO₄)₂·12H₂O and FeSO₄·7H₂O. The process was carried out at 90 °C (or 60 °C, laccase, and mixtures) for 1 h using a liquid ratio of 1:40. Then, the samples were washed with distilled water and dried (WTC binder oven) at 40 °C.

Dyeing - untreated and pre-mordanted samples were dyed by the exhaustion method with 3% (owf) of the natural dye madder with a liquid ratio of 1:40, at 90 °C for 1 h, followed by washing with distilled water and drying at 40 °C.

Colour evaluation - the colour strength (K/S) of the dyed fabrics was obtained using UV-vis spectrophotometer Shimadzu UV 2600 (Shimadzu, Kyoto, Japan), performing three measurements at different positions on the fabrics. K/S was calculated from the Kubelka-Munk equation, as in Eq. [1]:

$$K/S = \frac{(1-R)^2}{2R}, \quad [1]$$

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

Washing fastness - the evaluation of the washing fastness of the dyed fabric was performed accordingly to the ISO 105-C06 A1S standard. Then, the colour difference (ΔE) was determined using Eq. [2]:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}, \quad [2]$$

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 4 h at 50 °C using the QUV equipment (Q-Lab, Westlake, OH, USA), and the ΔE was determined using Eq. [2].

UV protection factor (UPF) - UPF measurement was performed on the UV-vis spectrophotometer, in the range of 290-400 nm. For each fabric sample, three measurements were performed, rotating the sample 90°. The UPF value for a flat, tension-free dry fabric is given by Eq. [3] (AS/NZS 4399):

$$UPF = \frac{\sum_{290}^{400} E_{\lambda} S_{\lambda} \Delta\lambda}{\sum_{290}^{400} E_{\lambda} S_{\lambda} T_{\lambda} \Delta\lambda}, \quad [3]$$

where, E_{λ} is the relative erythral spectral efficacy ($\text{W m}^{-2} \text{nm}^{-1}$), S_{λ} is the solar spectral irradiance (Melbourne), $\Delta\lambda$ corresponds to the measured wavelength range (nm) and T_{λ} is the spectral transmittance of the sample (%).

RESULTS AND DISCUSSION

Samples treated with laccase and *quebracho* alone showed a K/S similar to the control (Figure 1). After treatment with the metal compounds, there was an improvement in the K/S. Although the maximum K/S of the fabrics treated only with metals are similar, it was found that the Lac/Fe and Queb/Fe samples were superior to the others. Samples treated with laccase and metals showed a higher K/S than those treated with *quebracho*.

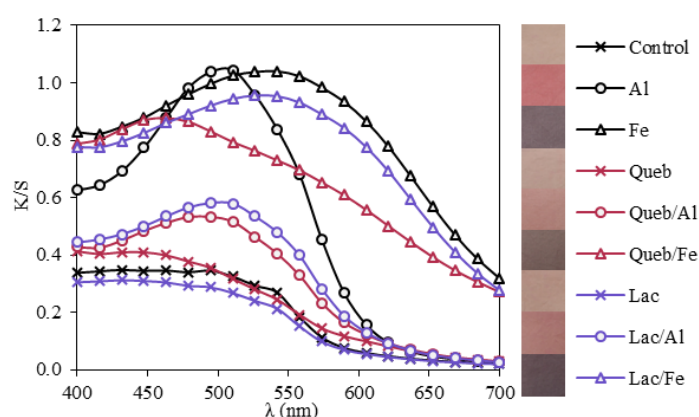


Figure 1. Colour strength (K/S) of the dyed samples.

Figure 2 shows the results of the washing and light fastness of the treated samples, as well as the respective UV protection factor.

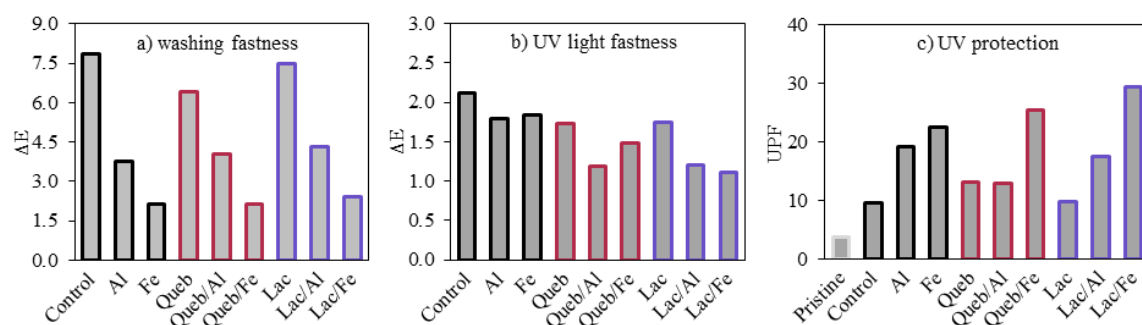


Figure 2. Washing fastness (a), UV light fastness (b), and UV protection (UPF) (c) of the dyed samples.

In general, the inclusion of the metals, in their form and together with the tannin and the enzyme, improved the properties under analysis. Iron-treated samples showed more favorable washing fastness results than other treatments. Both aluminum and iron treated samples showed better light fastness than untreated samples. However, the results were not promising when treatment with Queb/Fe was performed. This result was not what was expected, since other results in washing fastness and UPF are not accordant with the light fastness and further studies are required for a better understanding of this mechanism. In terms of UV protection, samples treated with Fe present better results when compared to Al [10]. In addition, Lac-Fe and Queb/Fe samples show good UV protection ($UPF=25-40$). This fact occurs due to the high value of K/S and indicates that the complexation between iron and tannin or

enzyme improved this property. In general, K/S, fastness properties, and UPF were improved after treatments with metallic mordants and biomordants [11].

CONCLUSION

The application of biomordants, such as *quebracho* and laccase, in the dyeing of cotton fabrics with madder extract seems to be a viable option to reduce the use of metallic mordants in the textile industry. The properties of washing and UV light fastness, UV protection, as well as K/S, were improved when the pre-treatment with the *quebracho* was performed. In the case of laccase, only an improvement in UV light fastness was observed. Nevertheless, the application of a small amount of metal salts with biomordants is necessary in order to achieve good UV light fastness and UV protection properties. Therefore, although it was impossible not to use metallic salts, the application of biomordants significantly reduced the need for their use.

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