SHORT COMMUNICATION

Copaifera langsdorffii Desf. bark extract: optimisation of dyeing conditions to wool and colour fastness properties

Patricia Muniz dos Santos Silva, Vitória Hamawaki França, Rayana Santiago de Queiroz, Fernando Soares de Lima, Harold S. Freeman, Silgia Aparecida da Costa and Sirlene Maria da Costa

aSchool of Arts, Sciences and Humanities, University of São Paulo, São Paulo, SP, Brazil; bLaboratory of Technical Textiles and Protection Products, Institute for Technological Research of São Paulo State, São Paulo, SP, Brazil; cWilson College of Textiles, North Carolina State University, Raleigh, NC, USA

ABSTRACT

The ability to add value to waste materials from industrial operations has come to the attention of the wood processing industry, with reports, for example, of extracts from the bark tree conveying colour and UV protection to textile fibres. The objective of the present work was to expand our developments in this arena by using Copaifera langsdorffii Desf. bark extract as a natural dye for textile dyeing. A complete $2^3$-statistical experimental design and the central point was elaborated. The results showed that the optimal dyeing conditions were 98°C, for 60 min, using undiluted bark extract. The dyed fabric was analysed by a spectrophotometer using the CIELAB system for evaluation of the colour strength. The results showed a K/S value of 5.78, and the dyed fabric had good colour fastness to rubbing and washing.

ARTICLE HISTORY

Received 11 September 2020
Accepted 4 January 2021

KEYWORDS

Natural dyeing; bark extract; wool; full factorial design; textile dyeing; colour fastness

1. Introduction

Increasingly, natural dyes have gained prominence as potential alternatives to synthetic dyes, because they are biodegradable, have low toxicity and generate low levels of allergic reactions (Yan et al. 2018). Identifying new plant species useful for the
extraction of natural dyes is important to enhancing the scope of natural dyes from different locations and source materials worldwide (Silva et al. 2020). In results from a study involving a comparison of fabrics prepared using conventional chemical and enzymatic methods, it was shown that the dyeing of xylanase enzyme treated fabrics led to enhanced uptake of dye in *Acacia catechu* extracts containing a mixture of saponins, flavonoids, glycosides, phenols, and terpenoids (Samant et al. 2020). In another study, waste material constituting the outer husk of chickpea was extracted and the liquid was used to dye textiles without the aid of chemical auxiliaries. The extract contained a mixture of terpenoids, glycosides, flavonoids, saponins, phenols, and tannins and gave higher affinity for protein fibres than cellulosic fibres (Jose et al. 2019). Related work involved the use of roasted peanut skin extract to dye cotton, silk and wool in the absence of mordants. While all three fabric types exhibited good dye-fibre affinity, dye uptake was higher the protein fibres than cotton (Pandey et al. 2018).

With the purpose of using waste as a source of natural dye, another idea has involved examining the utility of different tree barks in Brazil as substrates for textile wet processing. It is well known that various types of trees can be harvested for use in wood products and it is also known that their barks are invariably stripped away as wastes. As a starting point, we found that the *Croton urucurana* Baill. bark extract was suitable for textile dyeing, conveying colour and UV protection to textile fibres (Silva et al. 2020). Methods aimed at enhancing natural dye uptake on protein fibres have been examined. In one study, pinecone extracts were employed as a source of colourants for dyeing wool fabrics in the presence and absence of a mordanting agent. The beneficial effects of mordant choice on dye colour, fabric shades, and fastness properties were reported. It was also reported that the dyed samples have antibacterial properties, depending on the types of mordanting agent and bacteria used (Bahtiyari and Yilmaz 2018). Similarly, coconut coir (fibre) extracts were used as a source of colourants (e.g. tannin) in dyeing silk with the aid of microwave treatments and mordanting agents. It was reported that the use of acacia and turmeric as bio mordants considerably improved colour strength on silk. Further, tannin extracted from coconut coir produced a reddish-brown colour under the influence of microwave treatment (Kiran et al. 2020). In another study, wool fibres were dyed with colourants extracted from *Amebia euchroma*, cotton pods, and harmal seeds, using alum as the mordant and oxygenated plasma for surface modification of wool. Surface topography, morphology and chemistry of the wool fibres after plasma treatment were studied, and it was found that new oxygen-containing groups were produced on the surface of wool fibres after plasma treatment, along with surface etching and increased roughness of plasma-treated fibres. Increasing plasma treatment time improved the colour strength of samples dyed with extracts from *A. euchroma* and cotton pods but not from harmal seeds (Haji 2019). As an approach towards a more energy efficient extraction of plant-based Henna dye, ultrasonic and microwave extraction methods were developed. It was determined that these methods extracted Henna dye with in less time than conventional solvent extraction methods and that the resulting extracts gave dyeings on polyester fabrics having high colour strength and fastness properties (Rabia et al. 2019). In related work, plasma treatment of wool was used to enhance natural dye uptake and to lower the amount of mordants required in the dyeing process. ATR-FTIR, SEM, and AFM analysis of plasma-treated wool fibres confirmed significant changes in fabric surface chemistry and
topography. It was suggested that plasma treatment is a viable alternative to using potentially toxic metallic mordants (Haji 2020).

Because it has the greatest biodiversity in the world and has an extensive variety of plant species (Leite and Coradin 2011), Brazil has great potential for providing useful species to be considered as sources of natural dyes. For instance, *Copaifera langsdorffii* Desf., a tree of the Leguminosae family and Caesalpinioideae subfamily (known as ‘copaiba’ or ‘pau-d’óleo’) is a species native to Brazil and occurs in all regions of the country (Lorenzi 2002; Tobouti et al. 2017). It is a tree that has the possibility of multiple uses and can be considered a species of high social and economic value. It is widely known for the pharmacological properties of its component oleoresin, which is extracted from perforations that reach the heart of the trunk (Lorenzi 2002; Aldana et al. 2020). Studies also show a large amount of phenolic compounds in its leaves, with potential for use as an antioxidant and chelating agent, and a cytoprotective effect against heavy metal poisoning (Aldana et al. 2020). Studies also report the production of essential oils from its leaves, arils, fruits, root, wood and bark (Portella et al. 2015). In addition, its wood is suitable for civil construction, shipbuilding and furniture making (Lorenzi 2002). In the latter applications, its bark is stripped away as waste material. The ability to add value to waste materials from tree harvesting operations is a potential waste minimum through source reduction initiative. Tree bark can be harvested as illustrated in Figure S1. The extract from its bark has been used for dyeing cotton yarns by weavers from the Brazilian Cerrado (tropical savanna ecoregion) (Almeida et al. 2006). Use of tree bark in textile dyeing provides a practical way to convert an otherwise waste material into viable products.

Tree barks have different phytochemicals compounds, the amount and availability of which may vary with the species and the climatic and soil conditions from which the tree is found (Feng et al. 2013). Among these compounds, the main chromophores extracted are the phenolic compounds, such as flavonoids, stilbenes and tannins (Weigl et al. 2009). Carmo et al. (2016) showed that the *C. langsdorffii* bark has high content of chromogens that can be extracted with water, mainly flavonoids and tannins. Representative structures are presented in Figure S2.

The objective of the present work was to expand our studies in this area to the evaluation of *Copaifera langsdorffii* Desf. bark extract (cf. Figure S3) as a natural dye for textile fibres such as wool. The development and optimisation of dyeing conditions on wool was investigated using a full factorial design methodology with the independent variables: temperature, time and concentration of extract (cf. Table S1). Resistance to colour removal by (colour fastness to) washing and rubbing of the dyed fabrics was analysed.

2. Results and discussion

Figure S4 shows the resulting colours on wool fabrics (cf. Table S2 characteristics) by dyeing with the extract of *C. langsdorffii* bark. Table S3 shows the values of \(L^*, a^*, b^*\), chroma (\(C^*\)) and hue (\(h^*\)) from the colorimetric reading. Table S4 shows the composition of the runs of the factorial design and the experimental responses for the three repetitions of each run. The results of the reading in the spectrophotometer showed that the wool fabric dyed with the *C. langsdorffii* extract had a favourable increase in
colour strength (K/S) from 0.75 to 5.78. The highest colour strength value was obtained at 98 °C, for 60 min using 100% (undiluted) extract.

The data from the ANOVA are shown in Table S5. The p-value < 0.05 indicated which factors and interactions were significant (95% confidence level). From the experimental design study, all factors had a positive effect on the colour strength of the dyed fabric, which indicates that the level increase favours the increase in the colour strength of the dyed fabric. The highest impact was observed for the temperature factor, followed by the dye extract concentration factor. Figure S5 shows the Pareto chart. The bars that cross the vertical line show which ones are the significant factors, at the 95% confidence level. It is possible to observe that the temperature and concentration of the extract were the most significant factors in colour strength, followed by the second order interaction of these two factors. The time factor also has an influence on the colour strength, although a lesser effect when compared to temperature and concentration. The interaction between the three factors is not significant. Overall, the response surface plots (Figure S6) show that increasing any of the values of the variables - temperature, concentration and time - gave an increase in colour strength on wool fabric.

The results obtained in the present study illustrate the importance of dye concentration and elevated temperatures in dyeing textile substrates with tree bark extracts. Diffusion/penetration of large molecules such as tannin (MW 1,701) requires the level of fibre swelling that occurs above 90 °C. Besides that, the increase in temperature increases the kinetic energy of the dye molecules in the dyeing bath, as well as increases the swelling of the wool fibres, thus allowing more dye molecules to diffuse into the wool fibres (Haji and Rahimi 2020). The increase in temperature also decreases the amount of dye molecule aggregates, increasing the diffusion rate (Haji et al. 2020). However, elevated dyeing temperatures also increases the solubility of poly-hydroxylated dyes, making enhanced dyebath concentration necessary to build deep shades. In addition, by increasing the concentration of the extract, there is an increase in the dye molecules in the dyeing bath and, consequently, an increase in the adsorption of dye molecules to the surface of the wool fibres (Haji and Rahimi 2020). As the temperature and concentration of the extract are the factors with the greatest influence on the colour strength (K/S) in dyeing woollen fabric with the C. langsdorffii extract, when controlling these factors, it is possible to have greater control on the result of the colour strength.

The results obtained in the present study are comparable to the results of studies reported for dyeing textile substrates with other tree bark extracts. In the study by Punrattanasin et al. (2013) optimised silk dyeing with R. apiculata bark was obtained at 90 °C for 60 min at pH 3, using a dye extract concentration of 60%. The study carried out by Silva et al. (2020), indicated that the best dyeing with C. urucurana bark extract on cotton and wool fabrics was at 98 °C, 60 min and 100% of extract concentration.

The quality of dye penetration into wool fibres is reflected in the ratings of colour transfer due to rubbing (Table S6), which were good to very good (3–4 to 4–5). As expected, the lowest ratings were observed from the wet fabric rubbing. Colour change to washing was rated as average to good (3–4), indicating that there was a loss of colour intensity after washing. Fibre swelling during washing and concomitant disruption of dye—fibre interactions by water facilitate dye desorption/removal,
lowering dye depths on the fabric. The dyed fabric showed very good colour transfer fastness to rubbing with no colour transfer (5) to acetate, cotton and polyamide and very good fastness (4–5) with low colour transfer to polyester, acrylic and wool.

3. Conclusion
The *C. langsdorffii* bark waste material was found to be a potential natural dye source for wool fabric dyeing. The best dyeing conditions involved a dyeing temperature of 98 °C, a dyeing time of 60 min and the undiluted bark extract. In the dyeing, shades of brown and beige were obtained. The colour fastness ratings obtained were generally good to very good, with low colour transfer to rubbing indicated good dye penetration into wool fibres. It was also found that good resistance to colour removal upon washing was obtained without the use of a mordanting agent, indicating direct wool fibre affinity for the present natural dye.

Supplementary material
Includes experimental section, Figures S1–S6 and Tables S1–S6.

Disclosure statement
No potential conflict of interest was reported by the authors.

Funding
This work was supported by the Universidade de São Paulo (USP) under grant PUB 2017/2018; Institute for Technological Research of São Paulo State (IPT) and Foundation to Support Institute for Technological Research of São Paulo State (FIPT) under grant Programa IPT Novos Talentos n° 02/2015.

ORCID
Patricia Muniz dos Santos Silva http://orcid.org/0000-0003-3845-7463
Silgia Aparecida da Costa http://orcid.org/0000-0001-8331-538X
Sirlene Maria da Costa http://orcid.org/0000-0003-0522-0611

References
Aldana JA, De Grandis RA, Nicolella H, Guissoni APP, Squarisi I, Arruda C, Ribeiro VP, Tavares DC, Barcelos GRM, Antunes LMG, et al. 2020. Evaluation of cytoprotective effects of compounds isolated from *Copaifera langsdorffii* Desf. against induced cytotoxicity by exposure to methyl-mercury and lead. Nat Prod Res. 34(17):2528–2532.
Almeida CIM, Leite GLD, Rocha SL, Machado MML, Maldonado WCH. 2006. Fenologia e artrópodes de *Copaifera langsdorffii* Desf. no cerrado. Rev Bras Plantas Med. 8(2):64–70.
Bahtiyari MI, Yilmaz F. 2018. Investigation of antibacterial properties of wool fabrics dyed with pine cones. Ind Textila. 69(05):369–374.
Carmo JF, Miranda I, Quilhô T, Sousa VB, Cardoso S, Carvalho AM, Carmo FHDJ, Latorraca JVF, Pereira H. 2016. *Copaifera langsdorffii* bark as a source of chemicals: structural and chemical characterization. J Wood Chem Technol. 36(5):305–317.

Feng S, Cheng S, Yuan Z, Leitch M, Xu C. 2013. Valorization of bark for chemicals and materials: a review. Renew Sustain Energy Rev. 26:560–578.

Haji A. 2019. Application of D-optimal design in the analysis and modelling of dyeing of plasma-treated wool with three natural dyes. Color Technol. 136(2):137–146.

Haji A. 2020. Natural dyeing of wool with henna and yarrow enhanced by plasma treatment and optimized with response surface methodology. J Text Inst. 111(4):467–475.

Haji A, Ashraf S, Nasiriboroumand M, Lievens C. 2020. Environmentally friendly surface treatment of wool fiber with plasma and chitosan for improved coloration with cochineal and safflower natural dyes. Fibers Polym. 21(4):743–750.

Haji A, Rahimi M. 2020. RSM optimization of wool dyeing with *Berberis thunbergii* DC leaves as a new source of natural dye. J Nat Fibers. 1–14.

Jose S, Pandit P, Pandey R. 2019. Chickpea husk – a potential agro waste for coloration and functional finishing of textiles. Ind Crops Prod. 142:111833.

Kiran S, Adeel S, Yousaf MS, Habib N, Hassan A, Qayyum MA, Abdullah M. 2020. Green dyeing of microwave treated silk using coconut coir based tannin natural dye. Ind Tex. 71(3):227–234.

Leite LL, Coradin L. 2011. Introdução. In: Coradin L, Siminski A, Reis A, editors. Espécies Nativas da flora Bras valor econômico atual ou potencial plantas para o Futuro – Região Sul. Brasília: Ministério do Meio Ambiente.

Lorenzi H. 2002. Árvores brasileiras: manual de identificação e cultivo de plantas arbóreas no Brasil. Nova Odessa: Instituto Plantarum.

Pandey R, Patel S, Pandit P, Nachimuthu S, Jose S. 2018. Colouration of textiles using roasted peanut skin- an agro processing residue. J Clean Prod. 172:1319–1326.

Portella RO, Facanali R, Marques MOM, Rolim de Almeida LF. 2015. Chemical composition of essential oils from the vegetative and reproductive structures of *Copaifera langsdorffii* Desf. Nat Prod Res. 29(9):874–878. http://www.tandfonline.com/doi/abs/10.1080/14786419.2014.987145.

Punrattanasin N, Nakpathom M, Somboon B, Narumol N, Rungruangkitkriangkrai N, Mongkolrattanasit R. 2013. Silk fabric dyeing with natural dye from mangrove bark (*Rhizophora apiculata* Blume) extract. Ind Crops Prod. 49:122–129.

Rabia SA, Mazhar HP, Samad BA, Alvira AA. 2019. An efficient ultrasonic and microwave assisted extraction of organic Henna dye for dyeing of synthetic polyester fabric for superior color strength properties. Ind Tex. 70(4):303–308. doi:10.1080/15440478.2020.1821293.

Samant L, Jose S, Rose NM, Shakayawar DB. 2020. Antimicrobial and UV protection properties of cotton fabric using enzymatic pretreatment and dyeing with *Acacia catechu*. J Nat Fibers. 1–11. doi:10.1080/15440478.2020.1807443.

Silva PMDS, Fiaschitello TR, Queiroz RS, de Freeman HS, da Costa S, Leo P, Montemor AF, Costa S. 2020. Natural dye from *Croton urucurana* Baill. bark: extraction, physicochemical characterization, textile dyeing and color fastness properties. Dye Pigment. 173:1–14.

Tobouti PL, de Andrade Martins TC, Pereira TJ, Mussi MCM. 2017. Antimicrobial activity of copaiba oil: a review and a call for further research. Biomed Pharmacother. 94:93–99.

Weigl M, Kandelbauer A, Hansmann C, Pockl J, Muller U, Grabner M. 2009. Application of natural dyes in the coloration of wood. In: Bechtold T, Mussar K, editors. Handbook of natural colorants. Chichester: John Wiley and Sons.

Yan S, Pan S, Ji J. 2018. Silk fabric dyed with extract of sophora flower bud. Nat Prod Res. 32(3):308–315.