# ANTIBACTERIAL, UV PROTECTIVE AND ANTIOXIDANT LINEN OBTAINED BY NATURAL DYEING WITH HENNA

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Textile materials have become one of the functional needs of human beings and their multifunctional properties are highly demanded. Linen has been gaining rising interest and the multifunctional modification of this fiber can produce value-added textile products. In the present study, linen fabric was modified using natural dyeing with a combination of henna and copper sulphate. The resulting colored substrate was characterized using FTIR, TGA and SEM techniques. The color values of the dyed samples, for the various combinations of mordant and dye concentrations, were evaluated, along with the functional properties, such as antioxidant activity, antibacterial action and UV protection. The modified linen showed wash-fast coloration and displayed efficient protection against bacteria, UV light and free radicals. The multifunctional properties were retained after 20 washes. The henna-dyed linen can be claimed as a green multifunctional textile material that can be used for enhanced protection.

***Keywords***: linen, henna, dyeing, multifunctional

## INTRODUCTION

Textile materials play an important role in improving the quality of human life. In recent years, various functionalities of textiles have become hugely demanded. The driving forces for such demands are the increased awareness about the harmful effects of a variety of agents, such as bacteria, UV light, free radicals *etc*. and hence, the need for protection against them. Textile materials are widely studied for their modification using synthetic chemicals. However, some of the chemicals cause allergies and are not eco-friendly. User and disposal safety of such chemicals always remains a question.

With the changing fashion demands, the replacement of conventional cellulosic fibers has become a trend and linen has gained increased attention due to its higher moisture regain and better strength. Traditionally, textile dyeing and finishing are separate processes, while combined dyeing-finishing would be desirable as it would result in substantial savings in terms of water, energy, utilities *etc*. Natural compounds, such as henna, can be utilized for modification of linen for developing colored multifunctional material.

Henna (*Lawsonia inermis*) is also known as lawsone and, chemically, it is 2 hydroxy-1,4-naphthoquinone (hennotannic acid). It has a red-orange color and is generally extracted from henna leaves. As per CI classification, it is Natural Orange 6 with CI number 75480.[1] The active ingredient of henna leaves is lawsone, along with gallic acid, white resin, sugars, tannin and xanthones.[2] The application of henna for coloration of various textile fibers has been widely reported.[3-7] An interesting work in textile dyeing, dealing with the dyeing of polyester fiber using henna dye, without the use of metallic mordant, has been recently reported.[8]

Some other studies regarding the functional modification of textiles using henna are also available in the literature. Dev *et al*. studied the dyeing and antimicrobial properties of wool fabrics pretreated with chitosan and noticed an enhanced dye uptake and antimicrobial action.[9] Yusuf *et al*. reported on antimicrobial finishing of woolen yarn using an extract of henna leaves.[10] Nazari *et al*. investigated dyeing of wool using henna and walnut hull dye, and aluminium sulphate as a mordant, and found efficient moth-proofing of dyed wool fabric against *Dermestes maculatus*.[11] As cellulosic fibers are difficult to dye with natural dyes, as compared to proteinbased fibers, innovative methods, such as cationization of fabric, plasma treatment coating of fabric with chitosan, the use of enzymes and ultrasound during dyeing, to improve the dyeability have been reported.[12-14]

Linen is a fiber that has been gaining increased interest, and is now widely used for various products, such as garments, bed sheets and home textiles. Natural dyeing for multifunctional modification of linen has been reported to a limited extent. *Hubera nitidissima* (Dunal) Chaowasku (Annonaceae) was utilized as a dye for dyeing and antioxidant treatment of linen, wool and silk.[15] The effect of cellulase pretreatment on the dyeing properties and color fastness of linen fabric with chestnut shell extract was reported.[16] Grafting of linen fabric with monochlorotriazinyl-β-cyclodextrin to form an inclusion complex on the fiber and subsequent dyeing using *Allium cepa* anthocyanin extract, without any mordant, using both conventional and sonication dyeing methods, was reported.[17] Physicochemical characterization of thermally aged Egyptian linen dyed with organic natural dyestuffs was reported. These dyes were found to have a protective effect against thermal degradation of linen fabrics.[18] Dyeing and wicking properties of linen fabrics dyed using madder root, henna, buckthorn and walnut shell and metal mordants have been also investigated.[19]

To the best of our knowledge, the development of antioxidant, UV protective and antibacterial linen has not yet been reported using henna as a functional dye in the presence of copper sulphate as metallic mordant. Apart from this, the durability of such functional properties after subsequent washing treatment has been scarcely investigated. In the present research, simultaneous dyeing and functional finishing of linen fabric was performed. The efficacy of functional properties and their durability after repeated washing were also studied. Dyeing using henna proved to be an efficient tool for eco-friendly combined dyeing and finishing for linen fabric.

## EXPERIMENTAL

### Materials

Linen fabric (ready-for-dyeing, GSM-241.5, EPI-45, PPI-41) was supplied by Jayshree Textiles, India. Henna was purchased from a local market. The chemicals used in the study were supplied by Sigma Chemicals.

### Methods

***Dye extraction***

The extraction of the dye was carried out in water. In order to prepare a stock solution (5%) of henna extract, 5 g of henna dye powder was boiled in 100 mL of water for 1 h. This was followed by filtration of the extract. The final volume of the extract was brought to 100 mL using water.

***Mordanting and dyeing of linen fabric***

The mordanting and dyeing of linen fabric were carried out in a Rota dyer machine (Texlab, India), using a method described in the literature,[20] with slight modification. The liquor to the material ratio was maintained at 20:1. The linen fabrics were treated with a copper sulphate solution (1%, on weight of fabric) at room temperature and the temperature of the mordating bath was raised to 90 °C. The mordanting procedure was continued for 30 min. The mordanted fabrics were further dyed using the henna extract at 90 °C for 1 h. The dyed fabrics were washed with cold water for 10 min and dried.

***Characterization of modified linen***

The colored linen was characterized using FTIR (Shimadzu 8400s, Japan, 45-scans with a resolution of 4 $cm^{-1}$), thermogravimetric analysis (Perkin Elmer, USA), SEM (FEI Quanta, USA) and EDX techniques.

***Analysis of dyed fabrics***

*Color measurement*

The depth of color was estimated by the reflectance method on a Spectraflash SF300 (Datacolor International, U.S.A.). The K/S values were determined using the expression:

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

where R is the reflectance at complete opacity, K is the absorption coefficient and S is the scattering coefficient.

*Color fastness*

The dyed fabrics were evaluated for color fastness to washing (ISO 105C06-A1M method),[21] color fastness to rubbing[21] and color fastness to light.[21]

*Evaluation of functional properties*

The quantitative assessment of the antibacterial activity of the finished fabric was done using AATCC Test Method 100-2004.[22] The ultraviolet protection factor (UPF) of the dyed fabrics was evaluated on a Cary 300 UV-VIS Spectrophotometer (Cary, USA) as per AS/NZS 4399:1996 standard.[23] The antioxidant activity of the dyed fabric was evaluated using DPPH as reagent, as per a method reported in the literature.[24]

*Durability of multifunctional properties*

In order to evaluate the durability of functional properties, the dyed fabrics were washed as per ISO 105-CO6-1M test methods[21] and the washed fabrics were evaluated again with regard to their functional properties as per the methods mentioned above.

## RESULTS AND DISCUSSION

### Characterization of dyed substrate

Linen fabric is cellulosic in nature and processes like mordanting and dyeing can modify the structural characteristics of the fiber. As evident in Figure 1, no significant difference is observed in the FTIR spectrum of the dyed linen, compared to that of the undyed one. After dyeing, the carbonyl peak shifted to 1638 cm$^{-1}$, which might be attributed to the introduction of copper ions and the dye. The intensity of the peak at 3300 cm$^{-1}$ (OH stretching) increased after dyeing, which might be due to the introduction of lawsone, along with some polyphenolic compounds, into the dyed linen. The peak corresponding to C-H stretching vibration was observed at 2910 cm$^{-1}$, which also indicates the introduction of lawsone in the dyed fabric.

The effect of dyeing on the thermal characteristics of the fabric was studied by thermogravimetric analysis. Figure 2 clearly demonstrates an increase in the degradation temperature of linen after dyeing with henna.

The actual degradation of undyed reference linen started at 320 °C, while the dyed sample showed higher resistance to thermal degradation up to 350 °C. However, both samples showed a drastic weight loss after 350 °C, which was leveled off at around 450 °C. The final weight loss values at 800 °C were 94.16% for the reference and 84.37% for the dyed fabric, the dyed substrate presenting higher ash formation.

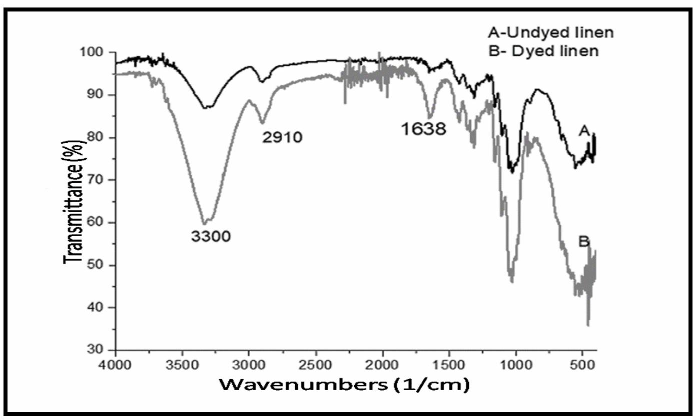


Figure 1: FTIR spectra of undyed and dyed linen

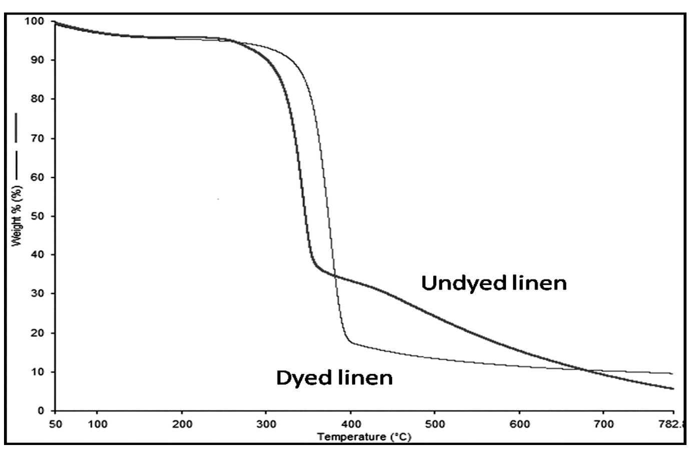


Figure 2: Thermograms of undyed and dyed linen (sample 4)

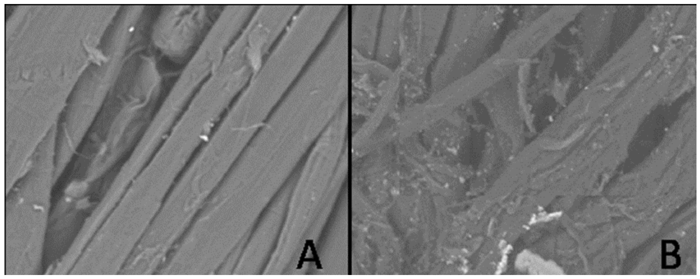


Figure 3: SEM images of undyed (A) and dyed (B) linen

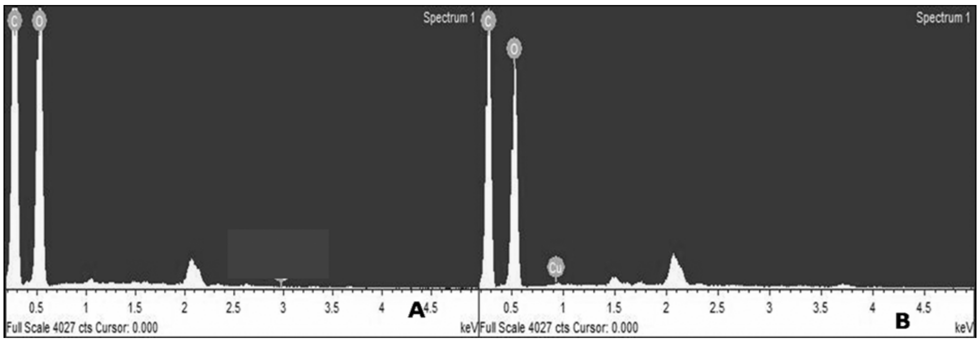


Figure 4: EDX analysis of undyed (A) and dyed (B) linen

SEM analysis shows no significant changes in morphology after dyeing. Some microparticles can be seen on the surface of dyed linen, which might be attributed to the presence of copper and dye. Limited reports are available in the literature regarding the role of henna extract as reducing and capping agent for the generation of nanoparticles in solution. Even though not reported so far, natural dyeing using henna can be claimed to be a route to achieve *in-situ* generation of metal micro/nanoparticles on the textile substrate. In Figure 3, micron-size particles can be seen deposited on the surface of the linen fabric.

EDX analysis (Fig. 4) of the dyed samples indicates the presence of copper, in contrast to the control fabric. This confirms the introduction of copper into the dyed fabric. No additional atom was expected to be introduced as a result of dyeing, as the extract of henna (including lawsone and polyphenolic compounds) is known to contain carbon, hydrogen and oxygen atoms.

**Analysis of dyed linen fabric**

The dyed linen fabrics were evaluated for color values and color coordinates, and the results are summarized in Table 1. As evident from Table 1, the color values increased with the increase in the dye concentration, at a constant mordant concentration. This may be attributed to the enhanced anchorage of the dye molecules on the fabric, as a result of increased absorption of copper ions. The hydroxyl groups of linen can hold copper ions up to saturation, when the optimum concentration of mordant is reached. The increase in depth is the combined result of the dye and the mordant, and it is obvious that the increase in the copper content on the fabric, as a result of mordanting, would induce higher dye attachment. The dyed fabrics displayed reddish-blue tones, the extent of which varied with mordant and dye concentration. The increase in mordant concentration resulted in bluer tones, while the increase in henna concentration led to redder tones.

Fastness properties, which represent the resistance of the dye on the fabric under the influence of external agents, were evaluated against washing, rubbing and light, and the results are summarized in Table 1. The linen dyed with henna without copper sulphate showed poor fastness properties, which were significantly improved with the use of the mordant. This highlights the role of the mordant in natural dyeing using henna. Washing fastness was improved with mordant concentration, generally, in the range from ‘good’ to ‘very good’. Dry rubbing fastness was ‘very good’ to ‘excellent’, while the ratings for wet rubbing were 1 grade lower. Light fastness was better (in the range from 'good' to 'very good') and was mainly due to copper, which is known to improve the light fastness of dyed fabrics.

Table 1
Color values of dyed fabrics

| Sample no. | $CuSO_4$ (%owf) | Dye (%owf) | K/S | Washing fastness | Rubbing fastness (dry) | Light fastness |
|---|---|---|---|---|---|---|
| 1 | 1 | 10 | 2.214 | 4-5 | 4-5 | 4 |
| 2 | 1 | 20 | 3.584 | 4-5 | 4-5 | 5 |
| 3 | 1 | 30 | 5.848 | 4-5 | 4-5 | 6 |
| 4 | 1 | 40 | 7.620 | 4 | 4 | 6 |

Table 2
Multifunctional properties of dyed linen

| Sample no. | Bacterial reduction (%) | | UPF | Antioxidant activity |
|---|---|---|---|---|
| | *S. aureus* | *E. coli* | | |
| Reference | N | N | 9.85 | - |
| 1 | 94.37 | 97.55 | 43.4 | 84.8 |
| 2 | 95.50 | 97.90 | 45.5 | 90.80 |
| 3 | 96.10 | 99.25 | 47.4 | 91.10 |
| 4 | 99.50 | 99.75 | 54.1 | 92.10 |

N – Negligible

**Multifunctional properties of dyed linen fabrics and their durability**

The antibacterial action, UV protection, antioxidant properties of the dyed samples were evaluated and presented in Table 2.

The functional properties imparted are the combined effect of the mordant–dye combination, as in the absence of the mordant, no permanent attachment to cellulose can be achieved. The dyed linen displayed efficient antibacterial activity against both gram-positive and gram-negative bacteria, which can be attributed to the presence of copper ions, as well as to henna. Both the mordant and the dye used here are known for their antibacterial activity and their combined effect was superior, as evident from Table 2. Bacterial reduction in the case of *S. aureus* and *E. coli* was of 99.5% and 99.75%, respectively, for sample 4. This can be considered as the best protection achieved on a textile support, taking advantage of the astringent properties of henna, which are mainly due to active components such as lawsone, gallic acid and tannins. Cellulose-based materials are generally prone to bacterial attack and can be protected from it using this method.

The UV protection of the fabric was improved with an increase in its color value, which might be also due to the combined effect of the mordant and the dye. The UPF values were improved with increasing mordant and dye concentration, and the optimum sample showed a UPF value of 45, which can be considered as efficient protection. As discussed in the UV-visible study, henna showed maximum absorption in the UV region, which can be a possible reason for the imparted UV protection. Copper ions and microparticles are also known for imparting excellent UV protection to textile substrates. The dyed linen also displayed efficient antioxidant property, which was found to increase with rising color value, as a result of increased dye concentration (reaching around 92.1% for sample 4). The antioxidant behavior can be attributed to the radical scavenging action of various components from the henna extract. Lawsone is a chemically 2 hydroxy-1,4-naphthoquinone, which is capable of absorbing and neutralizing free radicals through delocalization of the electrons in the system. The polyphenolic compounds in the henna extract acted synergistically to enhance radical scavenging. Free radicals are the basic cause of skin ageing and such modified substrates can help in radical scavenging, hence minimizing the ageing effect. The extract of henna also contains various polyphenolic compounds, which also show antioxidant activity. The dyed fabric (sample 4) was evaluated with regard to its functional properties after repeated washing (Table 3). The antibacterial activity decreased with each washing cycle and reached a moderate level after 20 washes. If the retention of 70% of the initial antibacterial activity is considered as standard, then, it can be claimed the fabric presented durability after 20 wash cycles. UPF values also showed a decreasing trend and reached value of 29.20 after 20 wash cycles, which can be taken as a moderate level of protection.

Table 3
Durability of multifunctional properties against repeated washing

| No. of washes | Bacterial reduction (%) | | UPF | Antioxidant activity (%) |
|---|---|---|---|---|
| | *S. aureus* | *E. coli* | | |
| 0 | 99.50 | 99.75 | 54.1 | 92.10 |
| 5 | 85.50 | 83.60 | 48.7 | 75.50 |
| 10 | 73.75 | 74.25 | 36.5 | 70.60 |
| 20 | 68.50 | 70.75 | 29.2 | 65.25 |

The antibacterial activity and UV protection displayed by the dyed linen was the combined effect of copper and henna, and thus in close relation with the color developed on the fabric. The color loss after each wash cycle resulted in a decrease in the efficacy of these functional properties. However, the dyed fabric retained its antioxidant activity after 20 wash cycles, and showed 65.25% radical scavenging.

## CONCLUSION

Multifunctional colored linen fabric was successfully achieved using henna dye. The dyed linen displayed efficient and durable antibacterial activity against *S. aureus* and *E. coli*. The dyed fabric also displayed better thermal stability, UV protective action and antioxidant properties. The modified linen fabric can be claimed as a suitable candidate for manufacturing protective textiles and apparels, especially, summer wear and hospital textiles.

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## REFERENCES

[1] F. Rehman, S. Adeel, S. Qaiser, I. A. Bhatti, M. Shahid *et al.*, *Radiat. Phys. Chem.*, **81**, 1752 (2012).
[2] R. G. Bhadane, N. S. Gaikwad, P. R. Girase and S. Pawar, *Pharm. Sci. Monit.*, **6**, 133 (2015).
[3] B. M. Badri and S. M. Burkinshaw, *Dyes Pigments*, **22**, 15 (1993).
[4] L.-F. Jia, *Wool Text. J.*, **11**, 21 (2008).
[5] M. Zarkogianni, E. Mikropoulou, E. Varella and E. Tsatsaroni, *Color. Technol.*, **127**, 18 (2011).
[6] H. Li, D. Zhao and R. Liu, *Adv. Mater. Res.*, **332-334**, 1276 (2011).
[7] J. Sheikh, P. S. Jagtap and M. D. Teli, *Fiber. Polym.*, **17**, 738 (2016).
[8] M. A. Rahman Bhuiyan, A. Ali, A. Islam, M. A. Hannan, S. M. Fijul Kabir *et al.*, *Fash. Text.*, **5**, 2 (2018).
[9] V. R. G. Dev, J. Venugopal, S. Sudha, G. Deepika and S. Ramakrishna, *Carbohyd. Polym.*, **75**, 646 (2009).
[10] M. Yusuf, A. Ahmad, M. Shahid, M. I. Khan, S. A. Khan *et al.*, *J. Cleaner Prod.*, **27**, 42 (2012).
[11] A. Nazari, *J. Text. Inst.*, **108**, 755 (2017).
[12] N. Baaka, A. Mahfoudhi, W. Haddar, M. F. Mhenni and Z. Mighri, *Nat. Prod. Res.*, **31**, 22 (2017).
[13] A. Haji, *Cellulose Chem. Technol.*, **51**, 975 (2017).
[14] I. Dumitrescu, P. S. Vankar, J. Srivastava, A. N. A. M. Mocioiu and O. G. Iordache, *Ind. Text.*, **63**, 327 (2012).
[15] M. Toussirot, W. Nowik, E. Hnawia, N. Lebouvier, A.-E. Hay *et al.*, *Dyes Pigments*, **102**, 278 (2014).
[16] Q. Zhao, H. Feng and L. Wang, *J. Cleaner Prod.*, **80**, 197 (2014).
[17] D. Coman, S. Oancea, N. Vrínceanu and M. Stoia, *Cellulose Chem. Technol.*, **48**, 145 (2014).
[18] N. Kourkoumelis, H. El-Gaoudy, E. Varella and D. Kovala-Demertzi, *Appl. Phys. A: Mater. Sci. Process.*, **112**, 469 (2013).
[19] M. Tutak, L. Önal and H. Benli, *Tekstil ve Konfeksiyon*, **23**, 374 (2013).
[20] M. D. Teli, J. Sheikh, M. Kamble and R. Trivedi, *J. Text. Assoc.*, **74**, 68 (2013).
[21] ISO Technical Manual, Geneva, Switzerland, 2010.
[22] AATCC Technical Manual, American Association of Textile Chemists and Colorists, 2007, 76, Research Triangle Park, NC AATCC.
[23] AS/NZS 4399, Sun protective clothing – evaluation and classification, 1996.
[24] J. Sheikh and I. Bramhecha, *Int. J. Biol. Macromol.*, **118**, 896 (2018).