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New Approach for Dyeing and UV Protection Properties of Cotton Fabric Using Natural Dye Extracted from Henna Leaves

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Abstract

A new approach for the dyeing and UV protection of cotton fabric using Henna extract was investigated. In this study, 3-chloro-2-hydroxy propyl, trimethylammonium chloride was used to substitute metallic mordants (heavy-metal salts) in the pre-treatment of cotton fabric. This will eventually prevent heavy metal pollution as well as facilitate dyeing without the addition of salt. Cationised cotton fabrics were dyed with Henna extract at different dyeing temperatures for different dyeing times. Colour strength, fastness properties (washing, rubbing and light), UV-blocking and tensile strength were investigated. Cationised fabric dyed with Henna extract exhibited outstanding enhancement in UV protection with minimal impact on the tensile strength. Enhancement or decrement in UV protection and colour strength was found to be governed by the dyeing temperature and dyeing time.

Key words: eco-friendly dyeing, natural dyes, henna extract, cationisation, UV protection.

ultraviolet radiation (UVR) such as fabric construction, chemical composition, textile auxiliaries, colour and the finishing process. Dyes often provide a good blocking effect against ultraviolet light transmittance, and the protection level rises with an increase in dye concentration. Light colours reflect solar radiation more efficiently than dark ones, allowing incident radiation to penetrate through the fabric with reflecting actions (scattering) [3]. Moreover most of the previous studies used synthetic dyes synthesised from petrochemical sources through hazardous chemical processes which pose a threat towards the environment and human body health [4].

Hence interest in natural dyes has increased considerably on account of their high compatibility with the environment, as well as the availability of various natural colouring resources such as from plants, insects, minerals and fungi [3]. It is reported that some natural dyes can not only dye fabrics in unique and elegant colors but also impart antibacterial and ultraviolet protective functions [5, 6].

Lawsonia inermis L., commonly known as “Henna”, is a shrub or small tree frequently cultivated in India, Pakistan, Iran, Afghanistan, Yemen, Egypt and Sudan. Powdered leaves of this plant are used as a cosmetic for staining hands and hairs. The dyeing property as well as UV absorption is attributed to the presence of Lawson; 2-hydroxy-1,4-naphthaquinone in Henna leaves [7]. This coloring component has the following structural formula, presented in **Figure 1**.

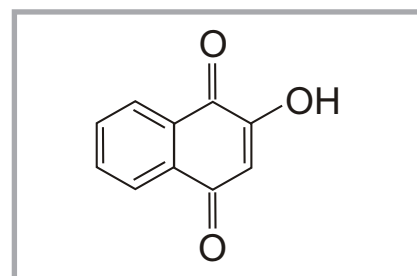


Figure 1. Structure formula of 2-hydroxy-1,4-naphthaquinone.

In the application of Henna to cellulosic textiles, fastness properties such as wash, light, perspiration, etc. are often very low. This may be due to the polar features of both cellulose and Lawson (hydroxyl groups are active sites), in addition to heterogeneity, diversity and a complexity of natural aspects. Therefore to overcome this drawback, additional treatments are often needed to enhance the durability value of textile products [4].

Many attempts have been carried out to elucidate the functional aspects of Henna dye as well as to enhance its fastness properties, especially washing and light fastness, by using several metallic mordants [7 - 10]

Cationisation is a novel treatment for cotton fabric which has been used to enhance the colour strength and fastness properties of dyeing. Cationic product 3-chloro-2-hydroxy propyl trimethylammonium chloride (CHPTMAC) is a relatively cheap, reactive and low toxic chemical which is potentially a good

Introduction

Protecting human skin against harmful UV radiation is an acute problem nowadays. Due to the decreased thickness of the ozone layer, more UV light reaches the ground. Long-term exposure to UV light can result in a series of skin diseases such as acceleration of skin ageing, photodermatitis (acne) and even skin cancer [1]. UV radiation consists of three ranges: UV-A (315 - 400 nm), UV-B (290 - 315 nm) and UV-C (100 - 290 nm). UV-C radiation is absorbed by the ozone layer, but UV-A and UV-B reach the earth's surface and cause serious health problems. Therefore the main UV radiations that should be blocked by textiles are UV-A and UV-B [1, 2].

Several factors affect the ability of fabrics to provide adequate protection from

cationic agent for the modification required [11].

What appears to be less emphasised in the literature is the application of natural dyes as a UV protection of cotton fabrics. In addition, the pretreatment of cotton fabric with cationic agents instead of metallic mordants can be a novel technique for upgrading the natural dyeing properties and minimising the pollution.

Accordingly the main objective of the present work is to dye cationised cotton fabrics with Henna extract without the addition of salt and determine the colour, fastness properties and UV protection of the dyed fabrics.

Experimental

Materials and chemicals

Scoured and bleached plain-weave cotton fabric of 117 gm⁻² was obtained from Hua Fang Co. Ltd., China. 3-chloro-2-hydroxy propyl trimethylammonium chloride was supplied by Aladdin Industrial Corporation, Shanghai. Henna powder was supplied by Tag Cosmetics Ltd. Omdurman-Sudan. All chemicals were used as received without further purification. Deionised water was used throughout the study.

Extraction of Henna dye

A certain amount of Henna powder was extracted in the required amount of water and boiled for 1h. The extract was cooled to room temperature and filtered to remove insoluble residues. The resulting filtrate was then used as stock dye solutions (1% extract) for subsequent dyeing experiments.

Cationisation of cotton fabric

Cotton fabric was cationised based on the pad-batch method. 50 g of 3-chloro-2-hydroxy propyl trimethylammonium chloride (CHPTMAC) was dissolved in 200 ml of deionized water. 22.8 g of sodium hydroxide was then added to form a 2,3-epoxypropyltrimethylammoniumchloride (EP₃MAC) solution, after which the fabric was impregnated with EP₃MAC solution at 50 °C for 20 min and then padded at a speed of 1 m/min and pressure of 1 kg/cm². The padded fabric was wrapped in a plastic film for 24 h at room temperature to prevent the migration of chemicals on the fabric and evaporation of water. After that, the fabric was rinsed twice with distilled water and neutralised with acetic acid solution (2 g/l). Finally the treated fabric was rinsed to obtain a pH of 7.2 on it and then dried in a commercial dryer at 60 °C [11].

Dyeing procedure

Cationised cotton fabrics were dyed with Henna dye solution without the addition of salt using the exhaustion method in a gy-12/HTAI-Hua Tai-China dyeing machine. Samples were immersed in a dye bath composed of Henna extract (1%) and sodium carbonate (15 g/l), using dye liquor ratio (1:20). All the dyeing experiments were carried out at temperatures of 40, 60, 80 and 90 °C and for 40, 60 and 80 min, respectively. Thereafter cotton fabrics were removed from the dye-bath and rinsed thoroughly in tap water followed by soaping (soap flakes 2 g/l, Na₂CO₃ 10 g/l, liquor ratio 1:30, 95 °C for 10 min). Afterwards the samples were washed and dried.

Test and analysis

X-ray diffraction

XRD patterns of normal and cationized cotton fabrics were recorded on an X-ray

diffractometer - D/MAX-2250 (Rigaku, Japan).

Colour strength (K/S value)

The colour strength of the dyed fabrics (K/S) was measured using a Datalog SP600⁺ spectrophotometer (Datalog Co. USA). K/S values were determined at the maximum dye absorption wavelength ($\lambda = 370$ nm).

Colour fastness to washing and rubbing

Washing was carried out in an SW-12A Tester to assess colour fastness to washing, (Wenzhou Darong Textile Instrument Co. Ltd. China) in accordance with the ISO 105-C10:2006 standard. The change in colour of specimens and stains of the adjacent fabrics were assessed with a Datalog SP600⁺ Spectrophotometer. Rubbing fastness was evaluated in dry and wet conditions in accordance with ISO 105-X12:2001.

Light fastness

The light fastness test was carried out using a Light Fastness Tester (ATLAS-150S⁺, USA) in accordance with ISO 105-B02: 1994, MOD. Samples were exposed to high intensity light for 50 h, and the degree of fading was assessed by the SDC blue wool scale.

UV-protection measurement

A spectrophotometer was used to evaluate the UV protection by measuring the Ultraviolet radiation transmittance value of each fabric across the wavelength range 280 - 400 nm, which includes UV-A and UV-B. The Ultraviolet Protection Factor (UPF) was obtained using an Ultra Violet Transmittance Fabric Analyser-Labsphere (USA).

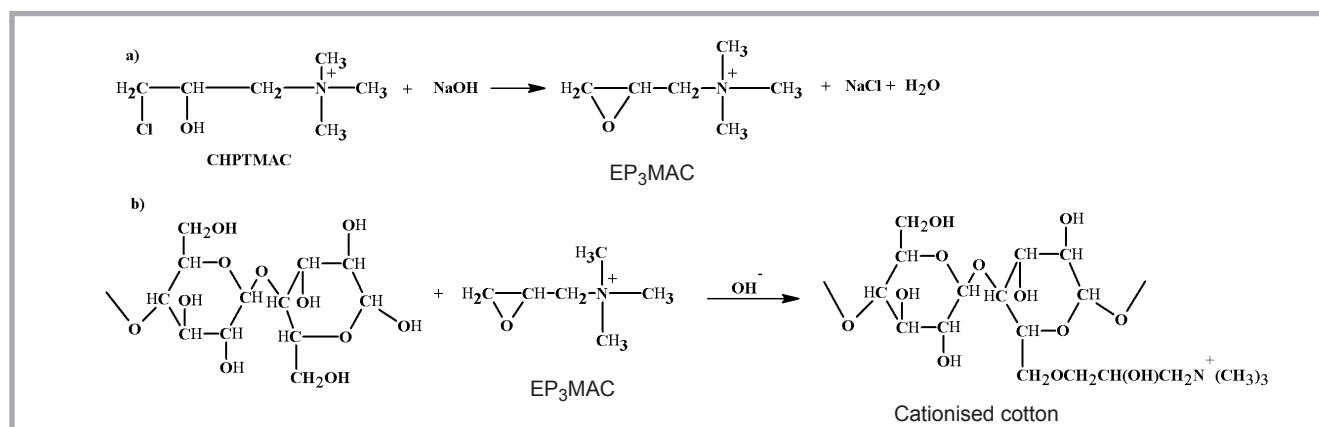


Figure 2. Reactions occurring during the cationisation process of cotton fabric. It is my own source.

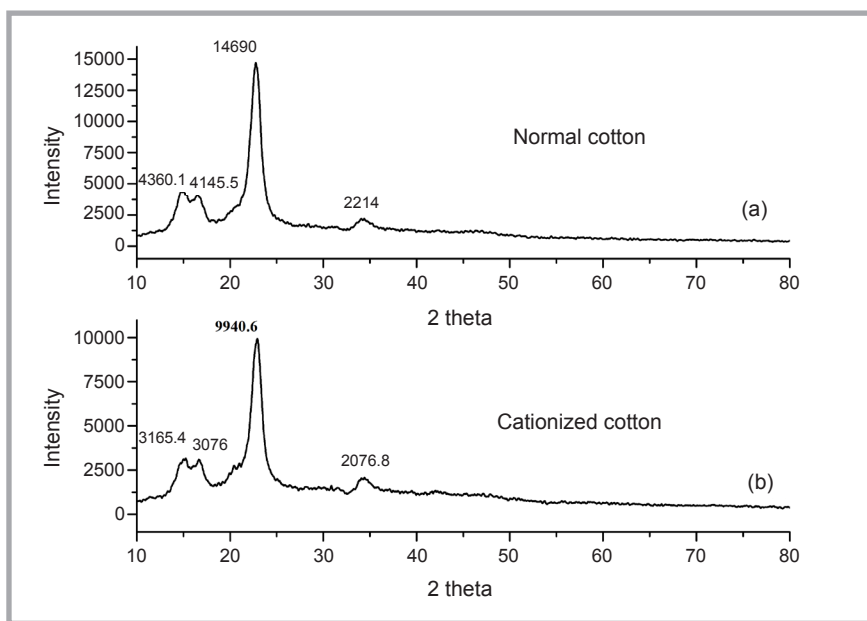


Figure 3. XRD pattern of (a) normal and (b) cationised cotton.

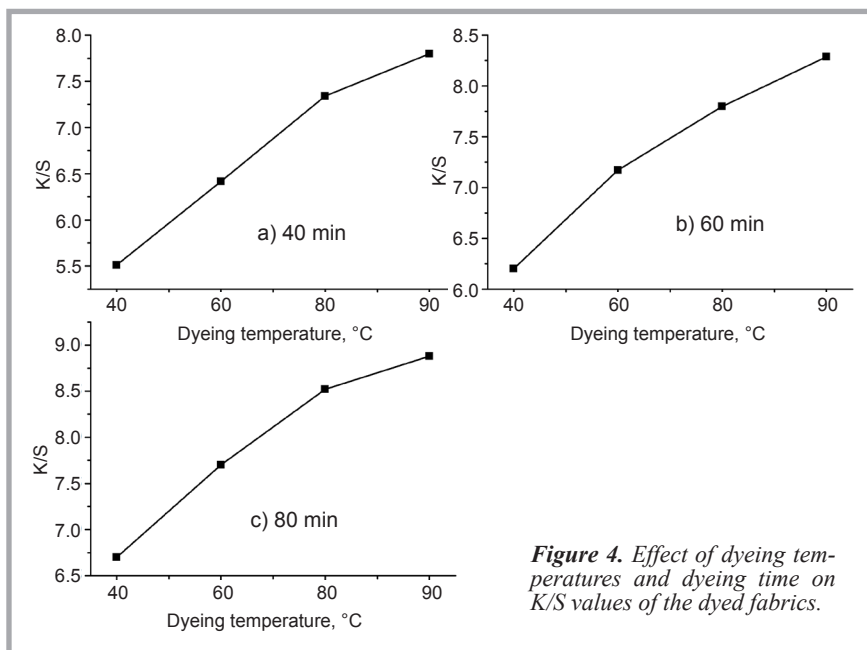


Figure 4. Effect of dyeing temperatures and dyeing time on K/S values of the dyed fabrics.

Tensile strength

The tensile strength was measured in the warp direction using a material testing machine - H10K-S (Tinius Olsen, U.S), according to ASTM-D5034-95. The data obtained were the average of three tests and reported as the average \pm standard deviation.

Result and discussion

Interaction of cationic reagent with cotton fabric

2,3-epoxypropyltrimethylammonium chloride (EP₃MAC) was prepared in situ by a reaction of 3-chlo-

ro-2-hydroxy propyl trimethylammonium chloride (CHPTMAC) with alkali (Figure 2, see page 61). EP₃MAC reacts with the hydroxyl groups of cellulose, creating cationic charges on the surface of cotton fabric [12]. As a result, cotton will have cationic dye sites covalently bound to the polymer chain. The carboxyl group in Lawson (appearing after adding alkali to the henna extract) which is negatively charged reacts with the cationic dye sites in the cotton fabric, enabling dyeing without the addition of electrolyte, which is normally needed to drive the dyes from the water onto the cotton fibre.

X-ray diffraction analysis

X-ray diffraction has been extensively used for investigation of the supramolecular order (crystallinity) of cellulose and its derivatives [13]. XRD patterns of normal and cationized cotton are shown in Figures 3.a and 3.b. It can be seen that normal cotton has main diffraction signals at $2\theta = 14.9^\circ, 16.55^\circ, 22.8^\circ$ and 34.05° [14]. These characteristic peaks also appear in the XRD patterns of cationised cotton, which reveals that the cationisation reaction does not change the main crystalline form of cotton samples. Meanwhile, in comparison with normal cotton, the peak intensity of cationised cotton declined due to the abundant -OH group in the texture of cotton being substituted by grafting of the cationic agent. The substitution of the hydroxyl group reduces the density of the hydrogen band [14].

Colour strength (K/S value)

The effect of dyeing temperature and time on the colour strength of the dyed samples is demonstrated in Figure 4. The colour strength (K/S) values were measured after dyeing of cationised cotton fabrics with Henna extract. The results obtained disclose that with increasing the dyeing temperature from 40°C to 90°C , the K/S values are enhanced, which reflects the positive impact of higher temperature on improving the swellability of cotton fabrics as well as the solubility of the Henna dye, thereby opening the cellulose structure and increasing the extent of penetration and diffusion of Henna dye molecules. In addition, the dyestuff is present in water as single molecules (ionized) as well as clusters of many molecules (aggregates) which are too large to enter the interior of the fibres at low temperature. Raising the temperature leads to the breaking down of the aggregates. Hence the number of single molecules existing in the solution increases. When a single molecule is absorbed by the fabric, additional monomers dissociate from the aggregates, which are, in turn, taken up by the fabric, resulting in a complete dyeing [8, 9].

The effect of the dyeing time on colour strength is also shown in Figure 4. With an increase in the dyeing time, more colour strength is observed. The less strength might be due to incomplete dyeing when insoluble impurities compete with the colorant to absorb onto the cotton fabric rather than the colorant. As the time

of dyeing increases from 40 to 80 min, more and more colour strength has been obtained, which might be because of the fact that the colorant gets significantly adsorbed and then absorbed [9].

Determination of fastness properties

Textiles are subjected to frequent washing, rubbing and light during usage. Therefore the durability of the finish applied on textile material to those conditions is extremely important and, hence, has been assessed, given in **Table 1**. Colour fastness to washing was assessed in respect of colour change and staining on multifibre fabric. Rubbing fastness was evaluated in dry and wet conditions.

As shown in **Table 1**, all Henna dyed fabrics have very good washing fastness regardless of the dyeing temperature and dyeing time. Change of shade and staining of adjacent fabrics (wool and cotton) were found to be good (3 - 4) to very good (4 - 5), respectively.

The dry rub fastness of all Henna dyed fabrics was good (4). Wet rub fastness

Table 1. Fastness properties of the dyed fabrics

Dyeing temperature, °C	Dyeing time, min	Colour change	Cross staining		Rubbing test		Light fastness
			cotton	wool	dry	wet	
40	40	4	4 - 5	4 - 5	4	3	3 - 4
40	60	3 - 4	4 - 5	5	4	3	3
40	80	3 - 4	4 - 5	5	4	3 - 4	4
60	40	3 - 4	4 - 5	4 - 5	4	3 - 4	4
60	60	4 - 5	4 - 5	5	4	3 - 4	4
60	80	4	4 - 5	4 - 5	4	3	4
80	40	4	4 - 5	4 - 5	4	3	4
80	60	4 - 5	4 - 5	4 - 5	4	3	4
80	80	3 - 4	4 - 5	5	4	3	4
90	40	4	5	5	4	3	4
90	60	4 - 5	4 - 5	4 - 5	4	3	4
90	80	4	4 - 5	4 - 5	4	3	4

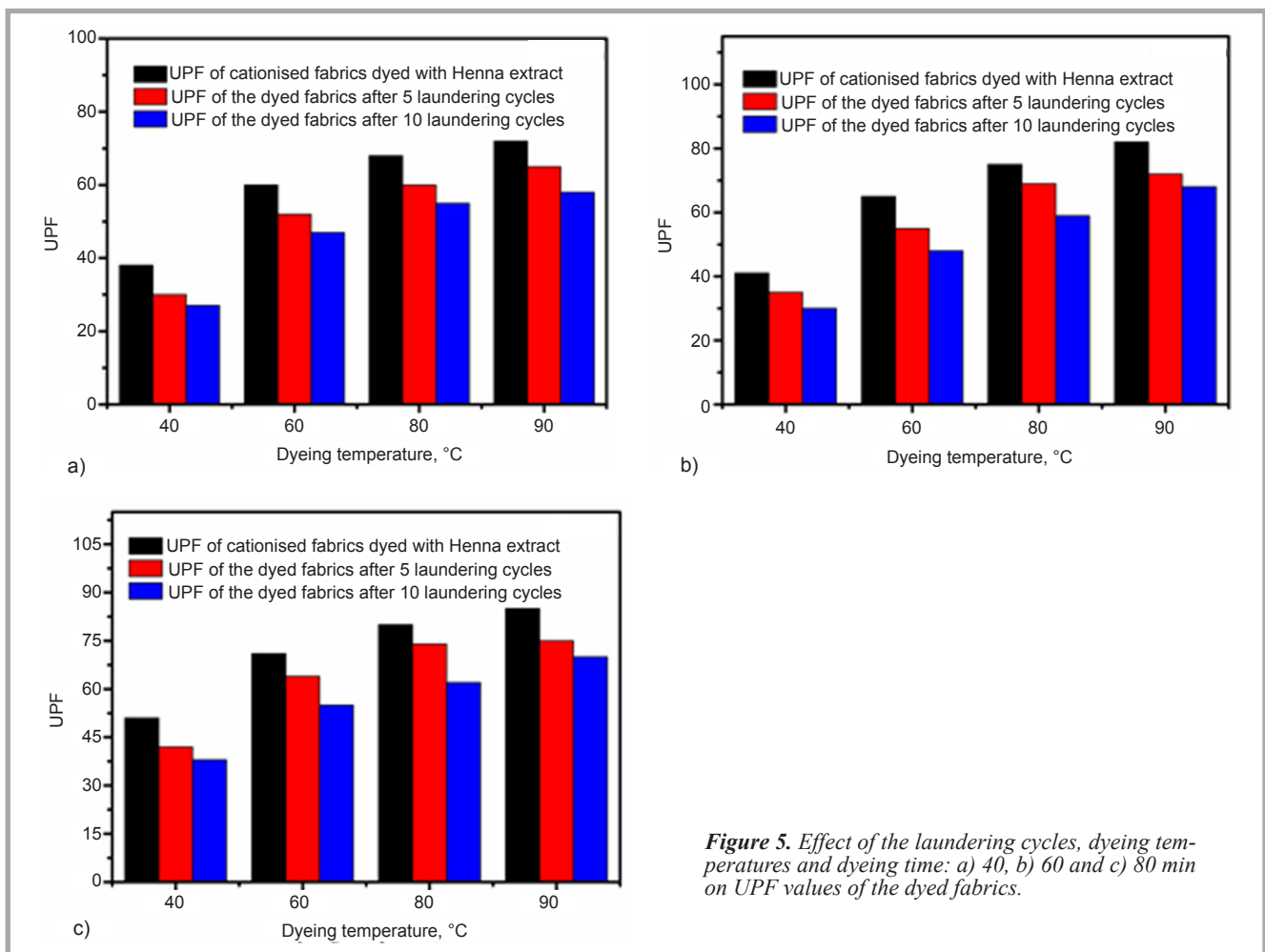
values were also found to be fairly good to good (3 - 4).

The durability of the dyed fabrics to washing could be attributed to the strong interactions between Henna dye and cationized cotton fabric.

As shown in **Table 1**, the light fastness property of all henna dyed fabrics was acceptable regardless of the dyeing

temperature and time, indicating that the presence of cationic groups in the molecular structure of cellulose enhances the swellability of the fibre (increasing the pore size), thereby encouraging the diffusion of dye particles inside the fibre pores and thus increasing the light fastness values [15].

It is observed from the data (**Table 1**) that the fastness properties of Henna dyed



samples are quite satisfactory for practical textile dyeing purposes. The results indicate that cationisation provided more dye sites and bears high colour depth. These can be explained on the basis that natural dyes contain ionizable groups (auxochromes) such as –OH. In aqueous solution at appropriate pH values, ionizable groups became soluble due to their conversion in anionic form, which can easily react with the cationic dye sites in cotton fabric, thereby improving the washing fastness property of the dyed fabrics. Moreover the link developed between Lawson and cationised cotton is supposed to be of high strength order, facilitating the colour fastness properties.

UV protection efficiency of dyed fabrics

The ultraviolet protection factor (UPF) of fabrics depends on the fibre content, weave, dyes used as well as finishing processes, and should be between 40 and 50+ to categorise clothing cotton fabrics with excellent UV protection. Based on these criteria, blank plain-weave cotton fabric with UPF rating 10 is classified as non-ratable fabric with inadequate protection for outdoor wearers [1].

As far as changes in UPF values as a function of the dyeing temperature and dyeing time are concerned, the results obtained (*Figure 5*, see page 63) disclose that increasing the dyeing temperature and dyeing time results in an enhancement of UPF values, thereby improving the extent of the UV-protection property of the dark shades obtained, which could be discussed in terms of a higher extent of blocking and/or absorbing harmful UV-radiation. These results indicate that dyeing fabrics in deeper shades improves

UV protection properties. K/S values of the dyed fabrics, which are a measure of the colour depth, seem to support the claim that higher colour depths increase UPF values [6]. Therefore it was proven that these results agreed with the previous data reported by Gies et al. [16] and Wislon et al. [17], who indicate that dyeing fabrics in a deeper shade improves their UV protection properties; although their studies were done with synthetic dyes. Also the results are in agreement with those of Feng et al. [18], who demonstrated that the UV protection properties of cotton fabric dyed with natural dyes (*Rheum and Lithospermum erythrorhizon*) using a metal mordant could effectively protect the skin from UVR.

To examine the washing durability, the dyeings achieved were subjected to 5 and 10 laundering cycles and then subjected to a UPF test according to the above-mentioned testing method. As shown in *Figure 5*, increasing the laundering cycles from 1 to 10 results in a slight reduction in UPF values of the dyed samples, which is indicative of good adhesion between the Henna dye and fabric surface. The durability of the dyed fabric to UV protection could be attributed to the strong interaction between cationised cotton and Henna dye.

Tensile strength

The influence of cationisation, dyeing temperature and dyeing time on the tensile strength of the dyed fabrics was investigated, corresponding data of which are given in *Table 2*. The tensile strength of all the dyed fabrics decreased compared with the control one. Sundaram et al. [19] confirmed cotton fibre strength reduction with chemical treatment. *Table 2* shows an overall decrease with an increase in the dyeing temperature and time, which may be due to fibre degradation at high temperatures and for longer time intervals.

Conclusion

Eco-friendly natural dyeing with UV protection was achieved by the cationisation of cotton fabric using 3-chloro-2-hydroxy propyl trimethylammonium chloride, followed by dyeing with Henna extract using very simple dyeing without the need for salt additions or mordants that might generate acidic media which

is harmful to cellulose and the environment.

The dyeing of cationised fabric with Henna extract resulted in ionic interaction and covalent linkages between cationised cotton fabric and Henna dye (Lawson), thereby improving the dyeing as well as fastness properties of the dyed fabrics. According to the findings of this work, the best dyeing conditions for considerably good UV protection and colour strength without affecting colour fastness properties and not adversely affecting fabric strength are (temperature: 90 °C and time: 60 min). Cationized fabrics dyed with Henna extract exhibited outstanding enhancement in UV protection with minimal impact on the tensile strength. Improvement decrement in UV protection and colour strength is governed by the dyeing temperature and dyeing time.

Finally, it can be concluded that the dyeing of cationised cotton with Henna dye is a very promising, eco-friendly and practical method for obtaining dyeing with outstanding protection against harmful UV radiation, without affecting other performance properties.



References

1. Alebeid Omer K, Zhao T. Anti-ultraviolet treatment by functionalizing cationized cotton with TiO₂ nano-sol and reactive dye. *Textile Research Journal* 2015; 85: 449-457.
2. Ibrahim NA, El-Zairy EMR, Abdalla WA, and Khalil HM. Combined UV-protecting and reactive printing of Cellulosic/wool blends. *Carbohydrate Polymers* 2013; 92: 1386-1394.
3. Grifoni D, Bacci L, Lonardo SD, Pinelli P, Scardigli A, Camilli F, Sabatini F, Zipoli G, Romani A. UV protective properties of cotton and flax fabrics dyed with multifunctional plant extracts. *Dyes and Pigments* 2014; 105: 89-96.
4. Lichtfouse E, Schwarzbauer J, Robert D. *Green Materials for Energy, Products and Depollution*. Ed. Springer, 2013, pp. 230-281.
5. Mongkholrattanasit R, Kryštůfek J, Wiener J, Víková M. UV protection properties of silk fabric dyed with eucalyptus leaf extract. *The Journal of The Textile Institute* 2011; 102: 272-279.
6. Mongkholrattanasit R, Kryštůfek J, Wiener J, Víková M. Dyeing, fastness, and UV protection properties of silk and wool fabrics dyed with eucalyptus leaf extract by the exhaustion process. *Fibres & Textiles in Eastern Europe* 2011; 19: 94-99.

Table 2. Tensile strength of dyed fabrics.

Dyeing temperature, °C	Dyeing time, min	Tensile strength, N
40	40	883 ± 31.4
40	60	880 ± 30.2
40	80	868 ± 29.1
60	40	795 ± 29.0
60	60	800 ± 29.7
60	80	794 ± 28.2
80	40	795 ± 29.5
80	60	785 ± 29.2
80	80	775 ± 29.6
90	40	780 ± 29.7
90	60	750 ± 29.7
90	80	720 ± 29.9
Reference cotton	-	986 ± 17.3

7. Rehman F, Shahid A, Summia Q, Ijaz BA, Muhammad S, Mohammad Z. Dyeing behaviour of gamma irradiated cotton fabric using Lawson dye extracted from henna leaves (*Lawsonia inermis*). *Radiation Physics and Chemistry* 2012; 81: 1752-1756.
8. Ibrahim N, Refaie R, Ahmed A. A new approach for natural dyeing and functional finishing of cotton cellulose. *Carbohydrate polymers* 2010; 82: 1205-1211.
9. Ali S, Hussain T, Nawaz R. Optimization of alkaline extraction of natural dye from Henna leaves and its dyeing on cotton by exhaust method. *Journal of Cleaner Production* 2009; 17: 61-66.
10. Iqbal J, Bhatti IA, Adeel S. Effect of UV radiation on dyeing of cotton fabric with extracts of henna leaves. *Indian J. Fibre Text. Res.* 2008; 33: 157-162.
11. Patino A, Canal C, Rodriguez C, Caballero G, Navarro A, Canal JM. Surface and bulk cotton fibre modifications: plasma and cationization. Influence on dyeing with reactive dye. *Cellulose* 2011; 18: 1073-1083.
12. Montazer M, Malek RMA, Rahimi A. Salt free reactive dyeing of cationized cotton. *Fibers and Polymers* 2007; 8: 608-612.
13. Cunha AG, Freire CSR, Silvestre AJD, Neto CP, Gandini A, Orblin E, Fardim P. Characterization and evaluation of the hydrolytic stability of trifluoroacetylated cellulose fibers. *Journal of Colloid and Interface Science* 2007; 316: 360-366.
14. Khalil-Abad MS, Yazdanshenas ME, Nateghi MR. Effect of cationization on adsorption of silver nanoparticles on cotton surfaces and its antibacterial activity. *Cellulose* 2009; 16: 1147-1157.
15. Micheal MN, Tera FM, Ibrahim SF. Effect of chemical modification of cotton fabrics on dyeing properties. *Journal of Applied Polymer Science* 2002; 85: 1897-1903.
16. Gies H, Roy C, Holmes G. Ultraviolet radiation protection by clothing: comparison of in vivo and in vitro measurements. *Radiation protection dosimetry* 2000; 91: 247-250.
17. Wilson C, Gies PH, Niven BE, McLennan A, Bevin NK. The relationship between UV transmittance and color-visual description and instrumental measurement. *Textile Research Journal* 2008; 78: 128-137.
18. Feng XX, Zhang LL, Chen JY, Zhang JC. New insights into solar UV-protective properties of natural dye. *Journal of Cleaner Production* 2007; 15: 366-372.
19. Sundaram V, Sreenivasan S. *Handbook of Methods of Tests*. Mumbai: CIRCOT (ICAR), 2004.

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