EFFECT OF NATURAL DYES AND DIFFERENT MORDANT TREATMENTS ON ULTRA-VIOLET PROTECTION PROPERTY OF COTTON FABRIC

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Received November 9, 2022

Natural dyes are eco-friendly, skin-friendly, have pleasing colours and other beneficial characteristics, such as UV protection property. In the present work, different natural dyes (onion skin, henna leaves, curry leaves, neem leaves and turmeric), along with a number of mordants (myrobalan, alum, ferrous sulphate and ferrous sulhate-myrobalan), were used to study their effects on colour strength and the ultraviolet protection factor (UPF) values of treated dyed cotton fabric. It was found that the highest colour strength (K/S) was achieved on ferrous sulphate-myrobalan treated turmeric dyed cotton fabric (75.45), followed by the samples dyed with onion skin (48.24), henna leaves (37.40), neem leaves (28.61) and curry leaves (25.96). The highest UPF value was found for ferrous sulphate-myrobalan pretreated curry leaves dyed cotton fabric (27.69), which indicated very good protection, whereas the ferrous sulphate-myrobalan pretreated onion skin dyed cotton fabric showed good protection (23.39), followed by those dyed with henna leaves (21.79), turmeric (19.48), and neem leaves (16.43).

Keywords: cotton, natural dyes, UV protection, mordanting, colour strength

INTRODUCTION

Recently, there has been an increase in public awareness about the side effects of UV radiation exposure and, as a result, the use of sunscreens on the parts of the body that are exposed to the sun has risen. In general, it is considered that clothing provides sufficient protection against sun radiation. However, this is not always true, particularly when using light garments.[1] Protection against solar UV radiation can reduce its effect, thus, a person's solar UV radiation exposure would remain between 1 and 10% of that without any protection.[2] Avoiding direct exposure to the sun and the use of protective clothing have been linked with reduced risk of developing both melanoma and non-melanoma skin cancers and other skin allergies.[3]

Basically, ultraviolet radiation (UVR) is an electromagnetic radiation, which we cannot see or feel, and it is emitted by the natural or artificial light sources. The natural source of UV radiation is the sun, which emits different types of electromagnetic radiation with different wavelengths and energies. The UVR spectrum can be subdivided into near UV (400–300 nm), middle UV (300–200 nm) and vacuum UV regions (200–10 nm) by physicists, or into UVA (400–315 nm), UVB (315–280), UVC (280–100 nm) and UVD (100–10 nm) regions by biologists. Of these, only UVA and UVB are of concern. UVA radiation is also known as glass transmission region, while ordinary glass blocks over 90% of the radiation below 300 nm and allows the radiation of about 350 nm to pass. UVA radiation is thought to contribute to untimely ageing and wrinkling of the skin, while it damages collagen fibres and destroys vitamin A in the skin. Today, it is well acknowledged that UVA radiation can generate highly reactive chemical intermediates, which indirectly damage the DNA and in this way induce skin cancer. UVB radiation is known as sunburn region and has been considered as the major cause of skin cancers, sun burning and cataracts.

The best way to avoid the effects of UVR is to cover the skin as much as possible with clothing. Clothing is made by different types of fabrics, which provide a simple and convenient protection against UVR, however not all fabrics offer sufficient UVR protection. According to the literature, the ultraviolet protection factor (UPF) of a fabric is highly influenced by its structure. It determines the inter-fiber gaps within the fabric, and thus the physical barrier that will oppose the passing of ultraviolet radiation.[4-6] The ultraviolet protection provided by clothing depends on the fabric construction, thickness, porosity and extension of fabric and its chemical characteristics, but also on the physico-chemical nature of the fibre, the dyeing and finishing treatments applied to the fabric, the moisture content of the fabrics and the presence of UV absorbers. Natural fibers, such as cotton, silk, and wool, have a lower degree of UV radiation absorption than synthetic fibers. Also, cotton fabrics show higher UPF as they contain natural impurities, such as pectin, waxes *etc*. Undyed or bleached fabrics offer much lower protection against UV radiation, if any, in comparison with dyed fabrics.

Dyes act like additives: they improve UV protection abilities, because they absorb UV radiation and visible light. It was noted that transmission/absorption attributes of dyes in the UV band were a better indicator of UV protection than the colour of the dyestuff itself. Dyes often offer a good blocking effect against ultraviolet light transmittance, and the protection level ramps up with an increase in dye concentration. The UPF also seems to be closely linked to the interaction of dye with the fibre. The same dye can give very different results on different fibres. The dyes used to color textiles can have a considerable influence on their permeability to ultraviolet radiation.[7] The use of dye or pigment, the absorptive groups present in the dyestuff, the intensity of the shade after dyeing, the evenness of dye penetration and the additives used in dyeing determine the ultraviolet protection efficiency of the textile materials. As a result, such dyes act as ultraviolet absorbers and increase the UPF of the fabric. The fabrics dyed with natural dyes have good ultraviolet protective properties and could absorb about 80% of the ultraviolet rays. The UV protective effect is strongly dependent on the absorption characteristics of natural dyes for UVR.[8]

Both synthetic and natural dyes can provide UV protection properties to fabrics. Most of the previous studies in this area have focused on synthetic dyes; however, the fact that they are synthesized from petrochemical sources through harmful chemical processes, which pose a threat towards the environment and human body health, represents a serious concern.[9] Given this, the interest in natural dyes has increased considerably in recent years, due to their high compatibility with the environment, ease of use, availability of various natural colouring resources, such as plants, insects, minerals and fungi.[10] It has been established that some natural dyes can not only dye fabrics in unique and elegant colors, but also impart antibacterial and ultraviolet protective functions.[11] Besides this, the application of natural dyes is on the rise due to the growing interest in environmental sustainability among consumers. Our previous study investigated the dyeing efficiency of onion skin dye on cotton textiles, under the effect of chitosan biopolymer used as mordant. The results showed efficient absorption (66.17%), colour strength (16.52) and wash fastness rating for the treated dyed cotton fabric.[12] In line with this, the present work was carried out to examine the suitability of a number of natural dyes for dyeing cotton fabric using different mordants to impart ultraviolet protection to the fabric. The color characteristics and ultraviolet protection properties were measured to determine the effectiveness of each treatment and dye.

EXPERIMENTAL

Materials

Cotton fabric

A survey was conducted in a local market in Hisar city of Haryana, and samples of different cotton fabrics most commonly used by consumers for apparel purposes were purchased. To confirm the purity of the fabrics, burning, microscopic and chemical tests were conducted. On the basis on these tests, pure cotton fabric was selected for further research work.

Natural dyes

Based on references found in the literature, seven dye yielding plants were selected, namely, onion skin, henna (mehandi) leaves, neem leaves, turmeric (haldi) powder and curry leaves were taken. Only renewable parts of the plant and waste parts were used: fresh leaves, flowers and vegetable residues were collected, washed to remove debris and dried in the shade. When completely dried, the materials were crushed into small pieces, pulverized into coarse powder and stored in air tight containers under controlled conditions until further use.

The plant powder samples were submitted to Fourier transform infrared spectroscopy (FTIR) analysis. The powder samples were prepared for analysis using the potassium bromide (KBr) pellet method.

Mordants

Natural mordants (myrobalan), as well as synthetic mordants (ferrous sulfate ($FeSO_4$), and alum ($AlK(SO_4)_2$) were investigated for improving the dyeing efficiency of different natural dyes.

Procedures

Preliminary treatment and analysis of cotton fabric

Enzymatic desizing and scouring

The selected cotton fabric was enzymatically desized and scoured to remove the starch and impurities, and make it more absorbent, so that it may better absorb the further finishing treatments. The cotton fabric was subjected to a desizing treatment using 0.5 mL/L Caprizyme AMY (Conc.) enzyme at 60 °C temperature for 60 min, at 1:20 material to liquor ratio, maintaining a pH of 7. The treatment liquor was drained out and the fabric was rinsed in hot and cold water, and then dried. Desized cotton fabric was scoured in a bath containing 0.4% (owf) Caprizyme Pecta enzyme, at 60 °C for 60 min, at a material to liquor ratio of 1:20 and pH 7.0. The fabric was rinsed in hot and cold water, and dried.

Characterization of fabric samples

After the desizing and scouring treatments, the fabric was assessed in terms of fabric count, weight, thickness and absorbency, according to standard procedures, as described below.

Fabric count: The fabric count is the number of warp (ends) and filling yarns (picks) per inch in a woven fabric. A Paramount pick glass, with a pointer, was used to determine fabric count in accordance with BS 2862:1957 standard test method.

Fabric weight: The samples were weighed separately on a Paramount precision scale, in grams per square meter, using ASTM-D 3776-90 test method.

Fabric thickness: Fabric thickness is defined as the distance between two parallel surfaces while exerting a specified pressure on the material. A Paramount thickness tester was used to determine the thickness of fabric according to BS 2544:1967 test method.

Drop absorbency test: The samples were tested as per AATC 79-2007 test method. The specimen was mounted in a hoop, the fabric should be free from wrinkles, and should not be too tense either. A burette was placed 9.5 mm above. A water drop was allowed to fall onto the specimen and the time until the drop lost its specula reflection was measured.

Aqueous extraction of dyes

Aqueous extraction is traditionally used to extract dyes from plants and other materials. The plant material was first broken into small pieces, powdered and sieved to improve the extraction efficiency (Table 1). The aqueous extract was prepared by soaking 10 g of plant powder in 100 mL of distilled water, in a stainless steel vessel overnight to loosen the cell structure. Then, the mixture was boiled at 80-85 °C for 1 hour to get the dye solution, allowed to stand till it reached room temperature and filtered to remove any plant remnants.

Dyeing of cotton fabric with natural dyes

The cotton fabric was treated with different mordants, *i.e.* myrobalan, alum, alum-myrobalan, ferrous sulphate-myrobalan, and then dyed with different natural dyes, *i.e.* curry leaves, henna leaves, onion skin, neem leaves, turmeric. The following procedures were used for dyeing of cotton fabric.

Accurately weighed cotton samples were introduced into the mordanting bath containing 3% of mordant (owf) in water. The treatment was carried out for 1 hour at 60 °C. The samples were then removed from the bath, squeezed and dried without washing. The dyeing of pre-mordanted cotton fabric was done with natural dye. The cotton fabrics were dyed with the dye extract at an M:L ratio of 1:30. Dyeing was carried out at 80 °C and continued for 1 hour.[13]

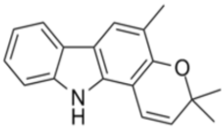
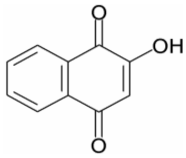
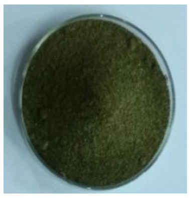
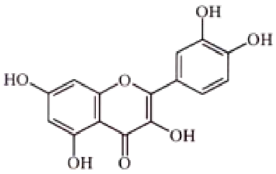
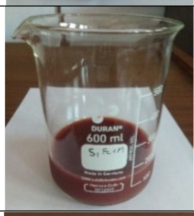
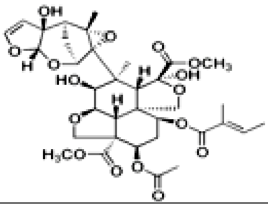
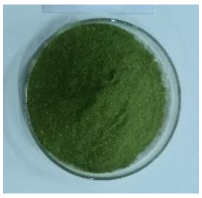
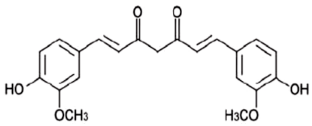
Colour analysis of dyed fabric

The colours of dyed samples were determined numerically using a computerized colour matching system. The reference spectra of dyed samples were observed by using an SS5100A Spectrophotometer; the K/S value and CIE LAB co-ordinates L*, a* and b* were noted down directly from the computer screen. This spectrophotometer uses the CIE LAB (1976) colour space, D65 illuminate matching and appraisal and 420 nm wavelength to measure the actual colour and change in colour. The Kubelka Munk Theory was used to predict the colour value:

$$K/S = (1-R)^2 /2R \quad (1)$$

The CIE LAB colour space uses L*, a* and b* scales to describe colour. L* is a measure of darkness/lightness of colour of an object and ranges from 0 (black) to 100 (white), a* measures redness (+positive a*) or greenness (-negative a*), b* – yellowness (+positive b*) or blueness (-negative b*), C* – dullness/brightness and H* is a measure of hue.

Table 1
Natural dyes used for dyeing cotton fabric

S.No.	Plant sources	Chemical structure	Dye powders	Dye extracts
1.	Local name: Curry Scientific name: *Murraya koenigii* Part used: Leaves			
2.	Local name: Henna Scientific name: *Lawsonia inermis* Part used: Leaves			
3.	Local name: *Pyaz* (onion) Scientific name: *Allium cepa* Part used: Skin			
4.	Local name: Neem Scientific name: *Azadirachta indica* Part used: Leaves			
5.	Local name: Turmeric Scientific name: *Curcuma longa* Part used: Tubers			

Ultraviolet protection property of dyed fabric

The UV protection factor (UPF) of the samples was determined in order to assess how efficiently the treated and dyed fabrics could protect the skin against UV radiation. The UPF of dyed experimental fabric was determined using an SDL UV penetration and protection measurement system (Compsec M 350 UV-Visible Spectrometer), according to the test method UVR Transmission AATCC-183:2004. The UPF was then computed as the ratio of erythemally weighted ultraviolet radiation (UVR) irradiance at the detector with no specimen to the erythemally weighted UVR irradiance at the detector with the specimen present.

Four specimens from each sample were tested. Specimens of 5 x 5 cm were cut from each sample, conditioned under standard atmosphere and placed against the sample transmission port opening in the sphere. UV transmission was taken with the specimen oriented in one direction, a second measurement at 0.79 rad (450) to the first and a third – at 0.79 rad (450) to the second. Individual measurements were recorded. Average spectral transmittance was calculated for the three measurements per specimen, with a total of five specimens representing each fabric sample. UPF was computed using mean percent transmission in the UVA range (320–400 nm) and mean percent transmission in the UVB range (280–320 nm).

The UPF of each specimen was calculated using the following equation:

$$UPF = \frac{\sum E\lambda \times S\lambda \times \Delta\lambda}{\sum E\lambda \times S\lambda \times T\lambda \times \Delta\lambda} \qquad (2)$$

where E λ = relative erythemal spectral effectiveness, S λ = solar spectral irradiance, T λ = average spectral transmittance of the specimen (measured), Δλ = measured wavelength interval (nm).

The UV protection category was determined by the UPF values described by Australia / New Zealand Standards AS/NZS4399 (1996), and given in Table 2.

Table 2
UPF rating and UPR protection category

UPF range	UPR protection category	UPF rating
15-24	Good protection	15, 20
25-39	Very good protection	25, 30, 35
40-50, 50+	Excellent protection	40, 45, 50, 50+

Wash fastness

Wash fastness tests were carried out as per the recommendations of IS: 3361-1979 method (BIS, 1979). Changes in colour of the dyed samples were assessed with grey scale no. 1, as per the recommendation of the ISO 105 method. The nine-step scale consisting of half fastness rating was used. The fastness rating of the specimen was the number of the grey scale, indicating a colour difference nearest in magnitude to the perceived colour difference between the original piece and the tested specimen. Also, the degree of staining on the bleached cloth was assessed with the help of grey scale No. 2 for staining.

Light fastness

Light fastness is defined as the resistance of a material to changing its colour characteristics as a result of exposure of the material to sunlight or an artificial light source. The fastness of the samples to sunlight was determined according to IS: 686-1985 method (BIS, 1985), and the samples were arranged on an exposure rack. The change in colour of the exposed portion was compared with that of the unexposed portion using the grey scale.

RESULTS AND DISCUSSION

Properties of desized and scoured cotton fabric

The selected cotton fabric was enzymatically desized and scoured to remove the starch and vegetative impurities from the fabric surface and to make it more absorbent, so that it could be more susceptible to further finishing treatments. Thereafter, the resultant fabric was assessed in terms of fabric count, weight, thickness and absorbency. The data obtained revealed that the initial grey cotton fabric used for the study consisted of 99 x 83 ends and picks per square inch, weighing 80 g/m^2 with the thickness of 0.19 mm. Meanwhile, the fabric after the desizing and scouring treatments had fabric counts of 100 x 84 and 102 x 85 ends and picks per square inch, weighing 79 and 72 g/m^2 with the thickness of 0.18 and 0.17 mm, respectively.

In the absorbency test, the scoured cotton fabric showed better water absorbency, compared to the initial grey fabric (Table 3). Enzymatic desizing and scouring play an important role in increasing the dyeing efficiency of cotton fabric, by enhancing its absorbency, without affecting other properties. As stated by Bahrum,[14] harsher chemicals used in conventional scouring cause strength loss of the fabric, compared to bioscouring. It is due to the fact that the bioscouring agent attacks the primary cell wall of the fibres, which is required for improved dye absorption, while conventional scouring agent attacks both primary and secondary cell wall and causes higher strength damage. Bioscouring also facilitates higher removal of pectin, causes more space in the fibres for dyestuff penetration, reaction and fixation in comparison to conventionally scoured fabrics.[14]

Effect of enzymatic desizing and scouring on whiteness and brightness indices of cotton fabric

After desizing and scouring, the whiteness, yellowness and brightness indices of the samples were assessed to ensure that uniform dyeing may be attained. The results are listed in Table 4. The data obtained reveal that, after enzymatic desizing, the whiteness index increased from 95.11 to 97.62, brightness – from 79.79 to 80.91, whereas yellowness decreased from -11.86 to -12.83. It can be further noticed from the table that, after enzymatic scouring, the whiteness index increased from 95.11 to 98.70, brightness – from 79.79 to 80.92 and the yellowness index decreased from -11.86 to -13.14. The maximum whiteness and brightness indices were obtained for enzymatically scoured fabric.

Table 3
Properties of desized and scoured cotton fabric

Samples	Properties			
	Fabric count (warp x weft yarns/sq. inch)	Fabric weight (g/m^2)	Fabric thickness (mm)	Water absorbency (min)
Initial (grey) fabric	99 x 83	80	0.19	5
Desized fabric	100 x 84	79	0.18	<1
Scoured fabric	102 x 85	72	0.17	<1

Table 4
Effect of enzymatic desizing and scouring on whiteness, yellowness and brightness indices of cotton fabric

Samples	Whiteness index	Yellowness index	Brightness index
Initial (grey) fabric	95.11	-11.86	79.79
Desized fabric	97.62	-12.83	80.91
Scoured fabric	98.70	-13.14	80.92

FTIR analysis of different natural dyes

FTIR analysis of onion skin, henna leaves, neem leaves, turmeric, curry leaves dye powders was performed and the spectra are shown in Figures 1-5. Figure 1 presents the spectrum of onion dye, with visible peaks at 3874.35, 3885.03, 3821.19, 3751.77, 3747.96, 3691.00 and 3675.45 cm^{-1} due to the hydroxyl groups (O-H-bending and –OH- stretch), the peak at 3447.59 cm^{-1} corresponding to the aromatic secondary amine, and the peaks at 1634.27 and 1618.60 cm^{-1} attributed to the C=C bond stretching vibrations in quinine or conjugated ketone. The peaks at 1558.84 and 1543.64 cm^{-1} indicate the presence of carboxylate (carboxylic acid salts). The peaks at 1472.67, 1426.90, 1406.92, 1361.19 and 1318.99 cm^{-1} suggest the presence of phenol or tertiary alcohol, aromatic ring, OH bend stretch, indicating characteristic water absorption. The peaks at 1084.51 and 1047.10 cm^{-1} indicated the presence of aromatic C-H in-plane bending. Finally, the peaks at 978.06 and 907.09 cm^{-1} exhibited the presence of C=C bending (alkene). These results are supported by Vankar *et al.*,[15] who stated that the colour of dyed fabrics depends on the nature of the chromophores, as well as the substituent functional groups, the auxochromes, of the dye molecular species.[15] Onion skin contains a dyestuff called 'Pelargonidin' (3,5,7,4 tetrahydroxy antocyanidol), as also pointed out by Zubairu and Mshelia.[16]

Figure 2 shows the spectrum of henna leaves dye: with a peak at 3447.60 cm^{-1} due to the hydroxyl group (H-bonded–OH- stretch), the peak at 2923.54 cm^{-1} corresponding to the methylene–CH- stretch and the peaks at 1591.48 and 1526.14 cm^{-1} attributed to the aromatic ring stretch. The peak at 1358.68 cm^{-1} indicated the presence of phenol or tertiary alcohol (OH bend). The peaks at 1184.35 cm^{-1} confirmed the presence of tertiary amine (CN stretch). Finally, the peaks at 1036.12 and 1008.05 cm^{-1} exhibited the presence of the aromatic C-H in-plane bend.

Figure 3 depicts the spectrum of neem leaves dye: the peak at 3457.47 cm^{-1} is due to the hydroxyl group (H-bonded–OH- stretch), the peak at 2111.31 cm^{-1} due to C=C stretching and the peak at 1626.21 cm^{-1} – attributed to alkenyl C=C stretch. The peak at 1597.09 cm^{-1} indicated the aromatic ring stretch (C=C-C). The peaks at 1400.97, 1353.29 and 1334.14 cm^{-1} suggested the presence of phenol or tertiary alcohol (OH bend). Finally, the peaks at 1173.34, 1130.39, 1105.07 and 1001.85 cm^{-1} demonstrated the presence of aromatic C-H in-plane bend. It was also reported by Tepparin *et al.* that tannins could improve the colour yield and colour fastness properties of dyed fabrics.[17] Antraquinone and flavonids help in imparting colour to any substrate. Moreover, the presence of these phytochemicals provide antimicrobial and antioxidant properties.[17]

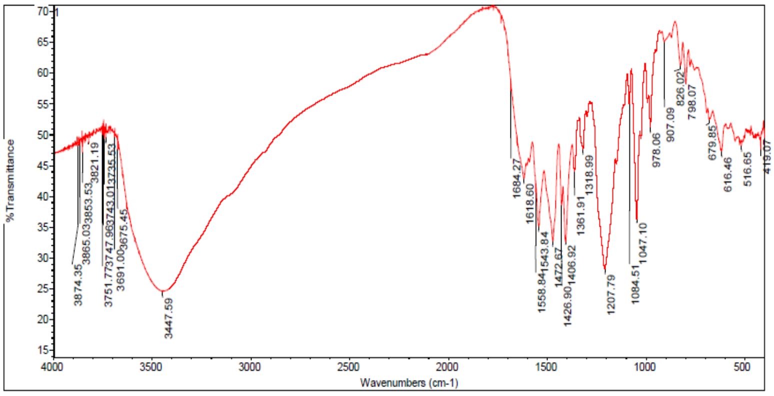


Figure 1: FTIR spectrum of onion skin dye

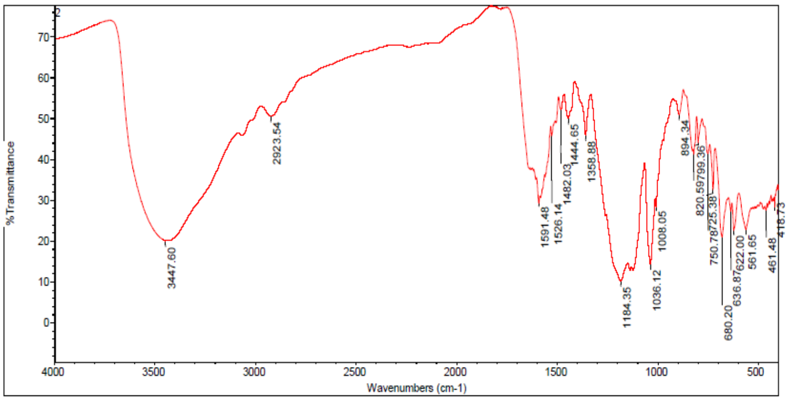


Figure 2: FTIR spectrum of henna leaves dye

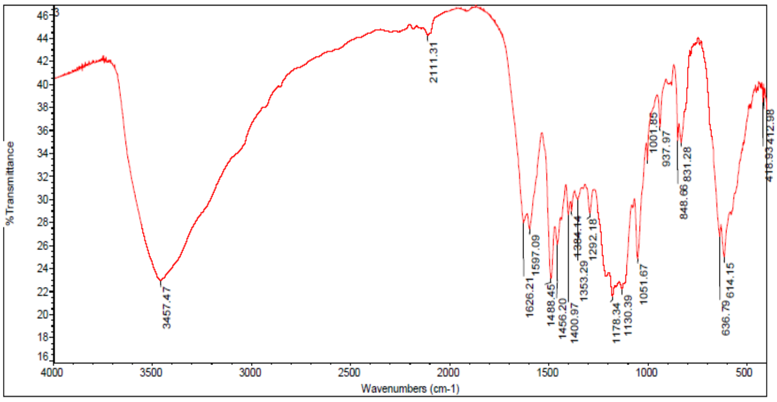


Figure 3: FTIR spectrum of neem leaves dye

Figure 4 presents the spectrum of turmeric dye, showing peaks at 3854.82, 3838.59, 3749.89, 3745.17, 3734.21, 3628.13 and 3445.98 cm^{-1} attributed to the hydroxyl group (H-bonded–OH- stretch), and peaks at 1598.61, 1538.99, 1503.17 and 1458.10 cm^{-1} indicating the presence of the aromatic ring stretch, while that at 1325.18 cm^{-1} was due to phenol or tertiary alcohol (OH bend). The absorption peak at 1209.41 cm^{-1} indicates the presence of tertiary amine (CN stretch). The peaks at 1129.93 and 1033.71 cm^{-1} confirm the presence of the aromatic C-H in-plane bend. Finally, the peaks at 916.03, 837.38 and 737.78 cm^{-1} exhibit the presence of C-H bending.

Figure 5 exhibits the spectrum of curry leaves dye represents the peaks at 3884.01, 3870.06, 3864.96, 3853.26, 3821.11, 3751.12, 3747.78, 3735.45, 3675.42 and 3339.06 cm^{-1} due to the hydroxyl group (H-bonded–OH- stretch), the peaks at 2919.05 and 2849.97 cm^{-1} corresponding to C-H stretching vibrations for saturated aliphatic group and the peak at 1633.85 cm^{-1} attributed to quinine or conjugated ketone. The absorption peaks at 1558.89 cm^{-1} and 1384.31 cm^{-1} indicated the carboxylic acid salts and phenol or tertiary alcohol (OH bend), respectively. The peak at 1070.78 cm^{-1} suggested the presence of the aromatic C-H in-plane bend. The presence of OH groups influences the absorbency of the dye material. The existence of phenol, tannin and quinone in some extracts was related to potent antimicrobial activities of some dyes.[18] Gawish *et al.* found that curcumin dye possessed the best antimicrobial and antimycotic activity due to the existence in their structure of methoxy and hydroxyl groups.[19]

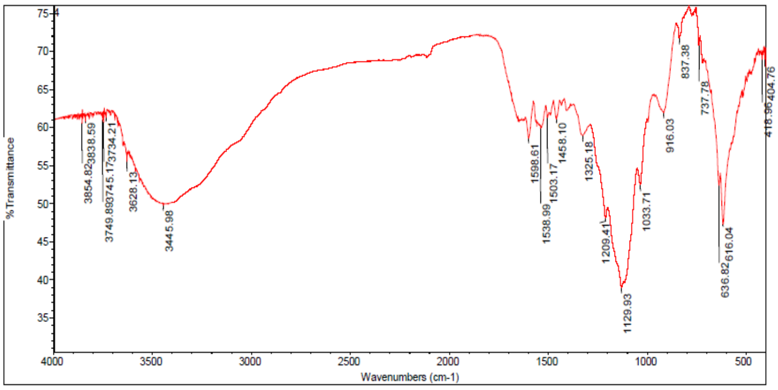


Figure 4: FTIR spectrum of turmeric powder dye

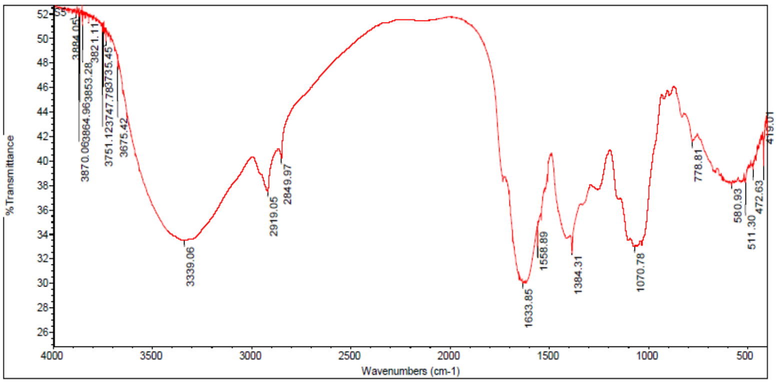


Figure 5: FTIR spectrum of curry leave dye

Combined effects of mordant treatments and different natural dyes on dyeing results and UPF of cotton fabric

In textiles, UPF is strongly dependent on the chemical structure of the fibres. Dyed cotton fabrics have been reported to show much higher UPF values, compared to those of undyed, bleached cotton.[20] In the present study, the natural dyes were used in combination with different mordants, being known that most natural dyes are better fixed using metal salts, such as alum, cuprous sulfate and ferric sulfate, in order to obtain complex compounds. The combined effect of the natural dyes with each of the mordants used on the K/S and UPF values of cotton fabrics was assessed.

Effect of natural dyes combined with myrobalan

It is clear from Table 5 that the maximum L* value (87.47) was observed for myrobalan treated turmeric dyed cotton fabric, followed by those dyed with curry (77.74), onion skin (76.08), neem (74.45) and henna (73.94) dyes. The a* value was found negative for all the myrobalan treated dyed cotton fabric samples, except for the onion skin dyed one, which indicated a redder tone of the dyed samples. The b* value was positive for all the myrobalan treated dyed cotton fabric samples, indicating a yellow tone. The C* depicted the chroma value, which was highest (44.09) for myrobalan treated turmeric dyed cotton fabric, followed by the samples dyed with curry (16.52), onion skin (15.63), neem (10.14) and henna (8.87). The hue angle (H*) was below 90°, with positive a* and b* values depicting the brown and yellowish khaki colour of myrobalan treated onion skin dyed cotton fabric, whereas the a* value was negative with a hue angle above 90° for myrobalan treated henna, curry, neem and turmeric dyed cotton fabrics (Fig. 6).

The highest colour strength (K/S) was noticed for myrobalan treated turmeric dyed cotton fabric (62.91), followed by onion skin (19.15), curry (11.17), neem (6.66) and henna (6.33) dyed samples. The colour strength value of naturally dyed cotton samples with mordanting treatment was quite good.

A higher UPF value was noticed for myroblan treated onion skin dyed cotton (17.08), followed by those dyed with curry (15.76), indicating good UV protection. Generally, natural dyes need assistance for their attachment to fabric fibers, and a mordant could be any one of several metal salts capable of providing a chemical bond between fiber and dye. Mordants bond with dyes more easily than the fiber, and improve the color strength and fastness of the dyed fabrics. However, myrobalan is a natural tannin-based mordant that has similar effects on cotton. The tannin it contains, along with the flavonoids and other phytochemicals present in the dyes, plays an important role in imparting and enhancing colour during the dyeing process. Similar results have been reported by Das *et al.*, who used onion skin for dyeing textiles, due to the pelargonidin (tetrahydroxy anthocyanidin) it contains in its structure, which acts as a colouring pigment.[21] Jadav and Gowda (2017) treated silk fabric with natural dye extracted from *Cichorium intybus* roots in order to produce a multifunctional textile material with antibacterial and antioxidant properties. The study revealed that mordants (alum and myrobalan) and mordanting methods have a synergistic effect on color strength, color fastness, antibacterial and antioxidant properties. Mordant treatment not only improved the color strength and color fastness properties of the sample, but also added to its antibacterial and antioxidant properties.[22]

Table 5
Combined effect of natural dyes and myrobalan on K/S and UPF values

Dyed samples	L*	a*	b*	C*	H*	K/S	UVA (%)	UVB (%)	UPF	Protection category
Onion	76.08	2.97	15.34	15.63	79.01	19.15	9.97	10.33	17.08	Good
Henna	73.94	-1.75	8.69	8.87	101.46	6.33	17.82	17.30	10.22	--
Curry	77.74	-2.63	16.31	16.52	99.21	11.17	10.14	11.24	15.76	Good
Neem	74.45	-2.45	9.84	10.14	104.04	6.66	15.15	14.98	11.73	--
Turmeric	87.47	-2.14	44.04	44.09	92.82	62.91	11.31	12.80	14.00	--

Onion skin   Henna   Curry   Neem   Turmeric

Figure 6: Myrobalan mordanted dyed cotton samples

Effect of natural dyes combined with alum

It is apparent from Table 6 that the maximum L* value (88.16) was observed for alum treated turmeric dyed cotton fabric, followed by the samples dyed with curry (78.07), onion skin (77.16), neem (74.57) and henna (73.84). The a* value was found negative for all the alum treated dyed cotton fabrics, except for the onion skin dyed sample, which indicated that the dyed sample had a redder tone. The b* value was positive for all the alum treated dyed cotton fabric samples, indicating their yellow tone. The C* depicts the chroma value, which was the highest (45.71) for the alum treated turmeric dyed cotton fabric, followed by those dyed with curry (19.90), onion skin (19.62), neem (11.02) and henna (9.40). The hue angle (H*) was below 90°, with positive a* and b* values depicting the brown and yellowish khaki colour of alum treated onion skin dyed samples, whereas the a* value was negative with a hue angle above 90° for alum treated henna, curry, neem and turmeric dyed cotton fabric samples, revealing a greenish khaki colour.

In terms of colour strength, the highest K/S value was found for alum treated turmeric dyed cotton fabric (71.26), followed by onion skin (21.59), curry (11.49), henna (6.72) and neem (6.08) dyed samples. The highest UPF value was found for alum treated onion skin dyed cotton fabric (16.72), followed by the turmeric dyed sample (16.24), indicating that these fabrics would provide good protection.

Other authors reported that the uptake of natural dye onto modified cotton fabric occurs through electrostatic interactions between the anions of the dye and the cationic segment on the modified cotton fibres.[23] Other mordants have also been investigated such as amla, babool, alum and tannic acid, during ultrasonic dyeing of cotton and wool fabrics with naturals dyes.[24] It was found that mordant treated samples have significant improvement in the dye absorption percentages. In addition, the fabrics dyed by ultrasonic dyeing methods showed deeper shades and good colour intensity.[24]

Table 6
Combined effect of natural dyes and alum on K/S and UPF values

Dyed samples	L*	a*	b*	C*	H*	K/S	UVA (%)	UVB (%)	UPF	Protection category
Onion skin	77.16	2.45	19.46	19.62	83.78	21.59	10.36	10.53	16.72	Good
Henna	73.84	-2.05	8.81	9.4	103.17	6.72	17.67	17.78	10.04	--
Curry	78.07	-2.94	19.68	19.90	98.53	11.49	11.63	13.05	13.57	--
Neem	74.57	-3.17	10.55	11.02	106.79	6.08	17.77	18.93	9.49	--
Turmeric	88.16	-2.00	45.67	45.71	92.55	71.26	9.58	11.11	16.24	Good

Onion skin Henna Curry Neem Turmeric

Figure 7: Alum treated dyed cotton samples

Effect of natural dyes combined with alum-myrobalan

The data in Table 7 reveal that the maximum L* value (69.21) was obtained for alum-myrobalan treated turmeric dyed cotton fabric, followed by those dyed with curry (48.66), onion skin (46.61), neem (45.02) and henna (44.86). The a* value was found negative for all the alum-myrobalan treated dyed cotton fabric samples, except for onion skin and turmeric dyed cotton fabric samples, which indicated their redder tone. The b* value was positive for all the alum-myrobalan treated dyed cotton fabric samples, which showed their yellow tone. The C*, the chroma value, was the highest (68.82) for alum-myrobalan treated turmeric dyed cotton fabric, followed by curry (23.73), onion skin (23.45), henna (17.85) and neem (17.83) dyed samples. The hue angle (H*) was below 90°, with positive a* and b* values depicting the brown and yellowish khaki colour of alum-myrobalan treated onion skin and turmeric dyed cotton samples, whereas the a* value was negative with the hue angle above 90° for alum-myrobalan treated henna, curry and neem dyed cotton fabric samples (Fig. 8). The highest colour strength (K/S) was noticed for alum-myrobalan treated turmeric dyed cotton fabric (66.18), followed by onion skin (20.22), curry (12.17), henna (10.37) and neem (8.73) dyed cotton samples. The highest UPF value was found for alum-myrobalan treated onion skin dyed cotton fabric (20.02), followed by curry (17.56), neem (16.43), and turmeric (15.06) dyes samples, indicating good protection.

Effect of natural dyes combined with ferrous sulphate-myrobalan

It is may be noted from Table 8 that the maximum L* value (67.93) was obtained for ferrous sulphate-myrobalan treated turmeric dyed cotton fabric, followed by the samples dyed with curry (57.64), onion skin (56.98), neem (54.97) and henna (54.72) dyes. The a* value was found negative for all the ferrous sulphate-myrobalan treated dyed cotton fabric samples, except for onion skin, henna and neem dyed ones, which indicated their redder tone. The b* value was positive for all the ferrous sulphate-myrobalan treated dyed cotton fabrics, indicating a yellow tone (Fig. 9). The C* value was the highest (42.31) for ferrous sulphate-myrobalan treated turmeric dyed cotton, followed by curry (14.05), onion skin (13.99), neem (7.93) and henna (7.64) dyed samples. The hue angle (H*) was below 90°, with positive a* and b* values depicting the brown and yellowish khaki colours of ferrous sulphate-myrobalan treated onion skin, henna and neem dyed samples, whereas the a* value was negative with a hue angle above 90° for the ferrous sulphate-myrobalan treated curry and turmeric dyed cotton fabrics.

Table 7
Combined effect of natural dyes and alum-myrobalan on K/S and UPF values

Dyed samples	L*	a*	b*	C*	H*	K/S	UVA (%)	UVB (%)	UPF	Protection category
Onion skin	46.61	7.02	22.38	23.45	72.55	20.22	8.74	8.65	20.02	Good
Henna	44.86	-1.18	17.81	17.85	93.83	10.37	13.05	11.18	14.73	--
Curry	48.66	-1.16	23.70	23.73	92.85	12.17	9.43	10.00	17.56	Good
Neem	45.02	-2.12	17.71	17.83	96.88	8.73	11.62	10.64	16.43	Good
Turmeric	69.21	4.90	68.82	68.99	85.88	66.18	10.61	11.88	15.06	Good

Onion skin Henna Curry Neem Turmeric

Figure 8: Alum-myrobalan treated dyed cotton samples

Table 8
Combined effect of natural dyes and ferrous sulphate-myrobalan on K/S and UPF values

Dyed samples	L*	a*	b*	C*	H*	K/S	UVA (%)	UVB (%)	UPF	Protection category
Onion skin	56.98	2.22	13.81	13.99	80.83	48.24	7.80	7.49	23.39	Good
Henna	54.72	1.94	7.39	7.64	75.21	37.40	8.70	7.98	21.79	Good
Curry	57.64	-0.50	14.05	14.05	92.10	25.96	6.11	6.32	27.69	Very good
Neem	54.97	1.08	7.85	7.93	82.12	28.61	11.62	10.64	16.43	Good
Turmeric	67.93	-0.72	42.30	42.31	91.02	75.45	8.67	9.07	19.48	Good

Onion skin Henna Curry Neem Turmeric

Figure 9: Ferrous sulphate-myrobalan treated dyed cotton samples

It was observed that the highest colour strength (K/S) was achieved for ferrous sulphate-myrobalan treated turmeric dyed cotton fabric (75.45), followed by onion skin (48.24), henna (37.40), neem (28.61) and curry (25.96) dyed cotton samples. The highest UPF value was found for ferrous sulphate-myrobalan treated curry dyed cotton fabric (27.69), indicating the fabric would provide very good protection, whereas the ferrous sulphate-myrobalan pretreated onion skin dyed cotton fabric – good protection (23.39), followed by lower, but still satisfactory UPF values of henna (21.79), turmeric (19.48), and neem (16.43) dyed samples.

These results are supported by those obtained by Bhattachararya and Shah,[25] who also reported the highest K/S values for ferrous sulfate and copper sulfate treated fabrics, which can be explained by the fact that these two mordants can form coordination complexes and readily chelate with the dyes. Since the coordination numbers of ferrous sulfate and copper sulfate are 6 and 4, respectively, some coordination sites remain unoccupied when they interact with the fiber. Hence, these metals can form a ternary complex on which one site binds with the fiber and the other site binds with the dye.[25] Also, in line with our findings, Mongkholrattanasit *et al.* reported that ferrous sulfate used as a metal mordant to pretreat fabric samples provided fabric with a UPF level that allowed them to be classified as offering "good UV protection".[11] The cotton fabrics dyed with natural indigo dye and mordanted with 10 g/L ferrous sulfate produced a greenish blue colour. The authors reported that the UPF values increased with an increase in the dye concentration. On the other hand, the undyed fabric and fabric dyed without mordant had low UPF values, which could not be rated as offering any degree of protection (less than 15).[11]

Colour fastness properties of dyed fabrics

Based on their higher colour strength (K/S) and UPF values, the ferrous sulphate-myrobalan mordanted dyed cotton fabrics were further tested to assess their fastness properties. The colour fastness properties of the samples, in terms of resistance to washing and light, are presented in Table 9.

As it is evident from the data in the table, the onion skin and neem dyed samples pretreated with ferrous sulphate-myrobalan had very good wash fastness rating (4/5) for colour change and good (4) for colour staining. The light fastness of the dyed samples pretreated with ferrous sulphate-myrobalan was also the highest (4/5) for the onion skin dyed cotton, whereas the lowest fastness rating was noticed for henna dyed fabric. The flavonoids found in onion skin are considered very useful during the dyeing process due to their ability to fix the dyes within fabrics.[26]

Table 9
Colour fastness rating of dyed fabrics

Ferrous sulphate-myrobalan treated cotton dyed with	Colour fastness grades		
	Wash		Light
	CC	CS	
Onion skin	4/5	4	4/5
Henna	3	3	3
Curry	4	4	4
Neem	4/5	4	4
Turmeric	4	4	4

CC = Colour change, CS = Colour staining

CONCLUSION

In this work, different mordant treatments were investigated to assist dyeing with natural extracts. Among these treatments, the ferrous-myrobalan treated and naturally dyed cotton fabrics showed the best results in terms of colour strength – 75.45 K/S for the turmeric dyed cotton, and in terms of ultraviolet protection – with very good protection (27.69) achieved for curry dyed cotton. The results of the study allowed concluding that natural dyes can be effectively used, when assisted by mordants, for achieving good dyeing results – high colour strength – and for imparting UV protection ability to cotton textiles in a sustainable manner. Such an approach may also impart multifunctionality to the textile materials.

ACKNOWLEDGEMENT: The authors would like to thank the Department of Apparel and Textile Science, I.C. College of Home Science, and CCS, HAU Hisar, for providing financial assistance and lab facilities for the research work.

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