MULTIFUNCTIONAL MODIFICATION OF KNITTED COTTON FABRIC USING POMEGRANATE PEEL WASTE

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The present paper reports on the development of multifunctional cotton fabric, using pomegranate peel extract. Cotton knit fabric was mordanted using zinc sulphate and dyed using pomegranate peel extract. Dye and mordant concentrations were optimized in order to get higher colour values. The dyed fabrics were evaluated for colour values, fastness properties and functional properties. Cotton fabric was imparted with antibacterial, UV protective and antioxidant properties, along with enhanced thermal stability, as verified using thermogravimetric analysis. Such multifunctional fabric can be an excellent candidate for sewing sports textiles and summer wear.

Keywords: pomegranate peel, dyeing, antibacterial, UV protection, antioxidant

INTRODUCTION

The utilization of waste materials for extracting useful chemicals is beneficial in terms of waste management and as a profit-yielding activity, considering the value-added products obtained from waste. Juice shops generate a huge quantity of fruit peels, which are rich in tannins, polyphenols, flavonoids, citric acid *etc*. These are high-value compounds that can be utilized in dyeing and functional finishing of textile materials.

Natural dyes include thousands of colorants obtained from plants or animals without any chemical processing. However, natural dyes have exhibit poor fixation to fabric substrates, so mordants are used. After combining with dye in the fibre, the mordant forms an insoluble precipitate and thus both the dye and mordant get fixed to become colour-fast to a reasonable extent. The mordant enters deeply into the fibre and combines with dyestuff to form the colour. Until the 19th century, people used natural dyes for colouring textiles. After the invention of synthetic dyes, the use of natural dyes was reduced due to the advantages of synthetic dye over natural dye with respect to application, colour range and fastness properties.[1-10] Nowadays, various synthetic dyes are utilized for colouration of cotton; however, some of these synthetic dyes/chemicals are harmful, *e.g.* azo dyes based on banned amines, allergic and carcinogenic dyes. A number of synthetic chemicals are also available for finishing, but user safety while using such compounds on textiles always remains a question. The best solution to such concerns is the use of natural dyes and chemicals. Some natural compounds possess functional properties and can be best utilized for simultaneous dyeing and functional finishing of textiles.

Dyeing textile fibres using natural dyes has been widely reported in the literature.[11-20] Natural dyeing using pomegranate peels has been explored on various textile fibres, such as cotton, wool, silk and Nylon 6.[6,16-20] These studies were mainly performed on woven fabrics. Simultaneous dyeing and multifunctional finishing of cotton knitted fabric using zinc sulphate and pomegranate peel extract has not been reported yet.

In the present work, pomegranate peel waste was utilized for simultaneous dyeing and multifunctional finishing of knitted cotton fabric. The concentrations of mordant and dye were optimized in order to get higher colour values and better multifunctional properties. The dyed fabric was evaluated for colour values and fastness properties. The efficiency of such knitted fabric as a multifunctional textile material was explored. All the functional properties obtained on cotton are desirable for summer wear (UV protection, antibacterial and antioxidant). Hence, the fabric dyed in accordance with optimum parameters can be used to manufacture naturally dyed multifunctional products for summer wear.

EXPERIMENTAL

Materials

Knitted cotton fabric (CPI-48, WPI-40, GSM-167.2) was purchased from the market, while pomegranate peels were collected from a juice centre. All the chemicals used were of laboratory grade and purchased from Sigma Aldrich.

Methodology

Extraction of dye from pomegranate peel

Pomegranate peels were dried in an oven at 50 °C for 24 h. The 10% stock solution of the dye was prepared by boiling 50 g of dried pomegranate peels in 500 mL water for 60 min at 90 °C. The extract was filtered and subjected to phytochemical analysis using a method described in the literature.[21-23] The extract was further used for dyeing.

Mordanting and dyeing fabric

Zinc sulphate was taken in different concentrations based on the recipe tabulated in Table 1. The mordanting of cotton knitted fabric was carried out in a shaking water bath (Julabo, USA), keeping the liquor to material ratio of 10:1. The fabrics were introduced into the mordant solution at room temperature and slowly the temperature was raised to 95 °C. The mordanting was continued at this temperature for 30 min. After mordanting, the fabric was squeezed and dyed using pomegranate peel extract as a dye (Table 1). The mordanted fabrics were introduced in the dyebath and dyeing was continued at 95 °C for 1 h. After dyeing, the fabrics were squeezed and washed with cold water. The mordant and dye concentrations were varied as summarized in Table 1.

Colour value by reflectance method

The dyed samples were evaluated for the depth of colour by the reflectance method using a 10 degree observer. The absorbance of the dyed samples was measured on a Spectraflash SF 300 (Datacolor International, U.S.A.), equipped with reflectance accessories. The K/S values were determined using the expression:

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

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

Table 1
Mordant and dye concentrations used for dyeing

Sample No.	Mordant (zinc sulphate) concentration (%)	Dye concentration (%)
Untreated	0	0
1	1	5
2	1	10
3	1	15
4	1	20
5	2	5
6	2	10
7	2	15
8	2	20
9	3	5
10	3	10
11	3	15
12	3	20
13	4	5
14	4	10
15	4	15
16	4	20

Dyed fabrics were simultaneously evaluated in terms of CIELAB colour space values (L*, a* and b*), using the Spectraflash SF300. In general, the higher the K/S value, the higher the depth of the colour on the fabric. L* corresponds to brightness (100 = white, 0 = black), a* to the red–green coordinate (+ve = red, -ve = green) and b* to the yellow–blue coordinate (+ve = yellow, -ve = blue). As a whole, a combination of these enables one to understand tonal variations.

Washing fastness

The evaluation of colour fastness to washing was carried out using ISO II methods.[24] A solution containing 5 g/L soap solution was used as washing liquor. The samples were treated for 45 min at 50 °C, using a liquor to material ratio of 50:1 in a Rota machine. After rinsing and drying, the change in colour of the sample and colour transfer onto undyed fabric samples were evaluated on the respective standard scales (rating 1-5, where 1 – poor, 2 – fair, 3 – good, 4 – very good and 5 – excellent).

Determination of antimicrobial activities of dyed fabrics

The antibacterial activity of the dyed fabrics was estimated by AATCC Test Method 100-2004.[25] The reduction in number of bacterial colonies formed, with respect to that on the untreated control sample, was estimated by using the following equation:

$$R = \frac{(B - A)}{A} \times 100 \tag{2}$$

where R = % reduction in bacterial count; A = the number of bacterial colonies recovered from the inoculated treated test specimen swatches in the jar incubated for 24 h contact period; B = the number of bacterial colonies recovered from the inoculated untreated control test specimen swatches in the jar immediately after inoculation (at “0” contact time).

UV protection factor (UPF)

The UPF of the functionalized fabrics was evaluated on a Cary UV-VIS 300 spectrophotometer (Cary, USA).

Antioxidant activity of fabrics

The antioxidant activity of fabric was evaluated using the 2.2-diphenyl-1-picryl-hydrazil (DPPH) reagent.[26,27] One inch square samples of wool were added to a test tube containing 3.5 mL of freshly prepared DPPH radical (1.0×10^{-4} mol/l) in a methanol solution and vortexed. Thereafter, the reaction was allowed to occur for 25 min at 25 °C in the dark, in a shaking incubator. The decolourisation of the samples was assayed at 517 nm and compared with a blind control containing DPPH in methanol (1.0×10^{-4} mol/l) without any sample.

$$\text{Antioxidant activity (\%)} = \frac{(Ac - As)}{Ac} \times 100 \tag{3}$$

where OD_{Sample} refers to the absorbance of the sample and OD_{Blind} refers to the absorbance of the blind control.

Thermogravimetric analysis

The thermograms of unfinished and finished fabric samples were recorded using an aluminum pan in the temperature range from 30 to 600 °C, and under inert atmosphere of N_2 at a flow rate of 50 mL/min (Perkin Elmer Thermo Gravimetric Analyzer).

Durability of multifunctional properties

The durability of multifunctional fabric properties to laundering was measured using washing conditions as per ISO 105-CO6-1M test methods.[28]

RESULTS AND DISCUSSION

Colour values and fastness properties of dyed fabrics

The dyed fabrics displayed yellow-brown shades, the depth of which varied with mordant and dye concentration. Representative samples were analyzed for colour values, the results being summarized in Table 2.

In general, the colour values increased with rising mordant concentration from 1 to 4%.

Table 2
Colour values and colour coordinates of dyed fabrics

Sample No.	a*	b*	L*	K/S	Washing fastness	
					Change in shade	Staining
4	1.030	22.616	78.770	1.27	4-5	4-5
8	0.288	23.789	78.391	1.29	4-5	5
12	0.173	24.066	77.453	1.33	4-5	5
16	-0.097	30.501	76.666	2.34	4-5	5

Table 3
Multifunctional properties of dyed fabrics

Sample No.	Bacterial reduction (%)		Antioxidant activity (%)	UPF (UV-C)
	S. aureus	*E. coli*		
Untreated	Negligible	Negligible	-	12.03
1	75.80	81.25	83.86	26.61
2	80.75	84.50	86.73	36.01
3	85.50	85.50	89.78	40.10
4	93.50	95.40	89.93	48.20
5	77.25	85.65	90.24	29.85
6	81.00	89.30	92.60	42.43
7	87.25	98.50	92.53	46.66
8	95.62	98.25	92.91	66.05
9	77.70	88.30	90.47	31.36
10	85.00	92.50	91.38	44.02
11	87.50	99.25	92.98	48.93
12	98.75	99.70	93.67	67.77
13	82.50	88.50	90.32	42.35
14	88.75	95.90	90.47	58.69
15	97.85	99.75	91.15	71.62
16	99.37	99.90	96.87	77.71

The lightness (L*) decreased with the increase in mordant concentration, obviously indicating an increase in colour depth with rising mordant concentration. The fabric exhibited an increase in greenness and yellowness, as represented by the decrease in a* and the increase in b*, with rising zinc sulphate concentration.

The resistance of the dye to washing is generally represented by washing fastness values. The washing fastness was evaluated and the results are listed in Table 2. The results clearly indicate excellent fastness properties in all the samples studied. The fabric showed negligible colour change after washing and staining to adjacent fabric was also negligible. This might be attributed to the efficient mordant action of zinc ions on the fabric. Zinc is known to form a complex with the dye extract, resulting in resistance to removal under the influence of washing liquor.

Multifunctional properties of dyed fabrics

The antibacterial activity of dyed fabric was evaluated against *S. aureus* and *E. coli* bacteria. As evident in Table 3, the fabrics displayed efficient reduction of bacterial colonies and hence efficient protection. In general, the dyed samples showed higher bacterial reduction of *E. coli*, as compared to that of *S. aureus*. When dye extract was applied without mordant, the dye was almost washed out in the absence of attachment points and such fabric showed no antibacterial action. In the presence of both mordant and dye, the samples showed excellent antibacterial action. Zinc is known for its antibacterial activity, while the tannins extracted from pomegranate peels are astringent. The available literature regarding the composition of pomegranate peel extract reports the presence of various phenolic compounds.[29-32] The phytochemical analysis also indicated the presence of polyphenolic compounds and flavonoids, which are known for their antibacterial activities. The combined effect was much superior and evident from Table 3.

UV protection is an important property required for garments to be used as summer wear. As evident from Table 3, the dyed fabric displayed excellent UV protection. The undyed fabric showed poor UV protection. The UPF values for the dyed fabrics varied between 26.61 and 77.71, mainly with respect to mordant and dye concentration. In general, the UPF values increased with rising mordant concentration, while keeping the dye concentration constant. However, the extent of increase was higher at higher mordant concentration. If the UPF values at 1% mordant concentration are compared (samples 1-4), an increment from 26.61 to 48.20 is remarked. Meanwhile, at 4% mordant concentration (samples 13-16), the UPF values varied from 42.35 to 77.71. This clearly indicates the role of mordant concentration in enhancing the dye uptake and, hence, the UV protection. Building up the shade is dependent on mordant and dye concentration, while their combined effect is expected to govern UV protection. However, no clear distinction was evident regarding the dominating effect of dye or mordant concentration on imparting UV protection to cotton fabric. The higher the mordant concentration, the higher amount of dye will be retained on fabric and the higher is the UV protection.

Also, almost all the dye-mordant concentrations investigated were found to be efficient with regard to the fabric's antioxidant activity. The tannins are known for their antioxidant activity and are widely used in cosmetics. The antioxidant activity was improved with the increase in mordant and dye concentration; however, the effect of dye concentration was much less pronounced from 5 to 20%.

Durability of functional properties

Durability towards washing is an important aspect of functional finishing, as it indicates the extent to which functional properties are retained after washing. Results in Table 4 indicate the effect of washing on the functional properties of multifunctional fabrics (sample 16).

As far as the antibacterial property is concerned, it was found to be decreasing with subsequent washes, reaching 72.15% reduction after 20 washes for *S. aureus* and 75.20% for *E.coli*. The antibacterial properties displayed by dyed fabrics, in the case of natural dyes, are the result of the combined effect of mordant and dye, and hence, the complex formed between them. After washing, some colourant might be lost due to breaking of the complex, which results in a decrease of antibacterial performance. However, the fabric can be called antibacterial after 20 washes, as it still displayed more than 70% reduction. UV protection showed a similar decreasing trend upon washing, as the UPF reached 25.50 after 20 washes, which can be considered a moderate level of UV protection. As some of the colourant, which was responsible for UV protection, was lost during washing, the UPF showed a decreasing trend. The knitted fabric structure also became loose because of abrasive washing under alkaline conditions, hence allowing more UV light to pass through it. Antioxidant activity also decreased upon subsequent washing, indicating loss of tannins and other natural colourants from the fabric. The antioxidant activity reached moderate levels after 20 washes, indicating 65.25% radical scavenging activity. The durability studies clearly indicate retention of all the functional properties to a moderate extent after 20 washes, hence indicating a semi-durable kind of multifunctional properties. This material is suitable for functional summer wear, where protection from UV light, microbes and radical-induced effects on skin is required.

Table 4
Durability of multifunctional properties of functionalized cotton (sample 16)

No. of washes	Bacterial reduction* (%)		UPF	Antioxidant activity (%)
	S. aureus	*E.coli*		
0	99.37	99.90	77.71	96.87
5	87.50	89.25	50.21	90.12
10	81.70	83.85	38.30	75.50
20	72.15	75.20	25.50	65.25

*represents average value of three determinations

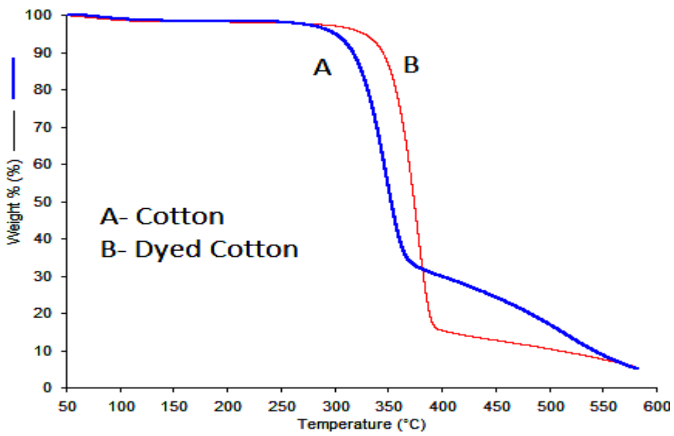

Figure 1: TGA curves of undyed and dyed cotton fabrics

Thermogravimetric analysis of dyed fabric

In order to study the evolution of thermal resistance after dyeing, thermograms were recorded and presented in Figure 1. As evident from Figure 1, the onset temperature (of degradation) was found enhanced in the case of the dyed fabric. This can be due to the protective effect of various components in pomegranate peel extracts.

The weight loss values were similar up to 300 °C; however, the weight loss values at 350 °C were very different. At 350 °C, the undyed fabric showed drastic decomposition, with 42.17% weight loss, while the dyed fabric exhibited weight loss values of 12.26%. The undyed cotton presented a sharp reduction in weight after 300 °C due to pyrolysis, resulting in the formation of levoglucosan. The continuous decrease in weight was evident after 350 °C, but it slowed down due to the formation of low molecular weight volatile compounds. The presence of metal ions and polyphenolic compounds resulted in an alteration of the thermal behaviour of the dyed cotton. The flame-retardant activity of the fabric treated with pomegranate peel extract was reported by other researchers.[33] They have reported the presence of oxygen (51.90%), carbon (28.70%), nitrogen (8.08%), potassium (5.60%), chlorine (2.24%), along with some trace amount of Cu, Zn, P, Na, Al, Si. The presence of such elements in the extract, along with that of aromatic phenolic rings, contributes positively towards increasing the thermal stability of treated textile substrates.

CONCLUSION

Green multifunctional modification of knitted cotton fabric was successfully carried out. The utilization of pomegranate peels for simultaneous dyeing and functional modification was reported. The dyed fabric showed good colour values with excellent fastness properties. The dyed fabric also displayed efficient antibacterial properties, UV protection and antioxidant properties. Thus, multifunctional summer wear can be prepared using pomegranate peel extract. These results clearly demonstrate that utilizing extracted natural colourants (pomegranate peel) as dyeing materials significantly facilitates obtaining high-quality antibacterial fabrics (~98%) with UV protection (UPF > 50) and antioxidant properties (>96%) of golden yellow colour. Therefore, the pomegranate peel dye has great potential to be used in manufacturing coloured multifunctional textiles.

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