UTILISATION OF CONICAL PRICKLES OF *BOMBAX CEIBA* BARK FOR MULTIFUNCTIONAL MOSQUITO REPELLENT COLOURATION OF COTTON

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The development of novel routes for the production of functional textiles is an urgent need. Natural dyes are a safe and sustainable choice for the colouration of textiles. To achieve the colouration of textiles with natural dyes, mordanting methods have been highly explored; the present work targets the functional natural dyeing of cotton by the *in-situ* development of azoic dye. The paper discusses a new application approach of a novel natural dye (derived from conical prickles of *Bombax ceiba* bark) to cotton using mosquito repellent ethyl anthranilate. The dye obtained from the extract of *Bombax ceiba* bark conical prickles (CPBCE) was further converted into azoic dye by reacting it with diazotised ethyl anthranilate. The developed coloured cotton fabric was endowed with mosquito repellence, antibacterial action, and UV protection. The colouration properties and fastness of dyed samples were examined using standard methods. Moreover, the dyed samples were also characterised using TGA (thermogravimetric analysis) and XRD (X-ray diffraction) analysis. Thus, 100% mosquito repellent properties, good antibacterial protection, and excellent UV protection were imparted to cotton.

Keywords: *Bombax ceiba*, mosquito repellent, antibacterial, UV protection

INTRODUCTION

Recently, increasing emphasis has been laid on producing non-toxic and environment-friendly dyes as an alternative to synthetic dyes.[1–5] Synthetic dyes are derived from crude oil derivatives that undergo extensive chemical processing, and the process releases harmful chemicals into water bodies, which is a severe cause of concern. Moreover, synthetic dyes produce challenging effluents, which are tough to treat and cannot be directly disposed of in the environment. With increasing interest in maintaining a healthy and pollution-free environment, safely dyed textiles are highly demanded. The strict rules and regulations imposed by the government regarding the harmful effects generated by textile effluents promote the utilisation of natural dye and dyed substrates. Various shades and hues can be easily obtained using synthetic dyes compared to natural dyes; still, the safe dyeing effects produced by the natural dyes is a motivation to explore them for commercialisation. Natural dyes are sustainable,[6] biodegradable, environment-friendly, and safe to the skin, and they also possess several pharmaceutical properties. However, natural dyes require the use of mordants to enhance their affinity towards textile substrates. Since, natural dyes have limitations of dull shades and poor fastness, metallic mordants are used to overcome these limitations. Metallic mordants are not always eco-friendly,[7,8] so bio-mordants are also used in place of harmful metallic mordants. Natural dyes are a rich source of phenolic compounds, and they can be reacted with diazotised bases to produce the desired colour through an azo-coupling reaction. In this way, a variety of shades can be developed by such an approach. Minimum studies have been done in this area.[9–12] In this context, our motivation has been to explore the azo-coupling reaction by using natural dyes.

Bombax ceiba (BC), also known as kapok or red silk-cotton tree, is mainly found in India, China, Pakistan, and Sri Lanka. It is widely used for medicinal purposes.[13,14] It possesses several properties, such as antioxidant,[15] antibacterial,[16] anti-inflammatory,[17] analgesic,[18] antiangiogenic,[19] antidiabetic,[20] hypoglycemic,[21] and hypotensive activities.[22] The chemical composition of the bark of BC consists of scopoletin, gallic acid, bomcibone, lupeol, glochidonol, alphitolic acid, salicylic aldehyde, quercetin, luteolin, and rutin.[23] Linen fabric was dyed using BC flowers, and multifunctional effects and colouration properties were explored.[24] Tamarind seed coats extract as a mordant and BC flower as a dye were used for the colouration of wool.[25] Gupta and co-workers developed multifunctional linen fabric using zinc oxide nanoparticles (ZnO), and a BC flower extract.[26] Conical prickles of *Bombax ceiba* bark (CPBC) were not explored till now in the colouration of textiles.

In the past few years, the rise in cases of mosquito-borne diseases has been a concern, and synthetic mosquito repellents are used to counter mosquito bites. Ethyl anthranilate is commonly found in citrus fruits, such as grapefruit and oranges, as well as in berries and starfruit, and is a non-toxic mosquito repellent. Ethyl anthranilate interferes in the host-seeking behaviour of mosquitoes[27] and shows superior mosquito repellent behaviour. It is used commercially in perfumes,[28] mosquito repellents,[29] and in the food industry.[28] Ethyl anthranilate is approved by the Food and Drug Administration (FDA) as an additive in food. Various interesting applications of ethyl anthranilate as a mosquito repellent are available in the literature,[9,30,31] however, its application has not been well made in the textile sector.

Azo dye belongs to a class of dyes having at least one (N=N) bond, which is generally connected to naphthalene or benzene rings. Azoic dyes are prepared on textiles by developing the azo group during the dyeing. The azo group is made by reacting a diazotised base with the couplers.

Very limited studies on the application of ethyl anthranilate to textiles have been found. To the best of our knowledge, the application of the extract of *Bombax ceiba* bark conical prickles (CPBCE), in combination with ethyl anthranilate, to cotton has not been documented so far. *Bombax ceiba* (BC) has many aromatic phenolic compounds, which can be used as coupler. In the present work, ethyl anthranilate was diazotised and used for azoic dye preparation. CPBC was solubilised, followed by application on cotton fabric, and the reaction was allowed to take place between the coupler and the diazotised base. The fastness and colouration properties of dyed cotton were explored to assess the successful dyeing of cotton. Functional effects (mosquito repellent, antibacterial, and UV protection) provided by dyed fabrics were analysed. The changes occurring after dyeing of the fabrics were evaluated using TGA (thermogravimetric analysis) and X-ray diffraction analysis.

EXPERIMENTAL

Materials

Woven cotton fabric having 72 PPI (picks/inch), 96 EPI (ends/inch), and 131.25 GSM (grams/square meter) was utilised for the experiments. CPBC was obtained from the textile chemistry lab of the Indian Institute of Technology (IIT), Delhi. The outside layer (bark) of the BC was dried in an oven at 50 °C for about 24 h and crushed to a fine powder. Ethyl anthranilate, acetic acid, sodium acetate, sodium nitrite and hydrochloric acid (36%) were obtained from Tokyo Chemical Industry.

Methods

Dyeing of cotton fabric using azoic dye derived from BC

Ethyl anthranilate (5 g) was dissolved in 100 mL of H_2O containing 7 mL of HCL (36%). The solution was cooled to 0-5 °C, and 2.4 g of $NaNO_2$ was added to it. The reaction mixture was then allowed to complete the diazotisation for 4 h. The required amount of sodium acetate was added to the reaction mixture (pH: 4.5–5). Lastly, an appropriate quantity of distilled water was added to the reaction mixture to get a solution of 0.7% (w/v).

Fine powder of CPBC (15 g) was boiled with 7.5 g of NaOH for 1 h at 90 °C in 100 mL of water. Then, it was filtered to remove the undissolved particles, and 100 mL of solution was made by adding the desired quantity of water. The CPBC dye solution was applied on cotton fabric at various concentrations (on the weight of fabric) using a shaking bath. A liquor ratio of 1:20 was used, and the application of dye was carried out for 1 h at 90 °C, with a dosing of sodium chloride (exhausting agent) of 15% on the weight of the fabric (owf).

The treated fabric was further squeezed and used directly for the *in-situ* coupling reaction at 40 °C for 1 h in a shaking bath. The concentrations of both components are tabulated in Table 1. Cold washes with water and dilute hydrochloric acid were given to dyed fabrics. Furthermore, soaping of dyed fabrics using non-ionic soap (2 gpl) was done at 60 °C for 15 min.

Evaluation of colour of dyed fabric

Colour parameters of the dyed fabrics, such as colour strength (K/S) and colour values (L*, a*, b*, C*), were measured using a spectrophotometer (Color-Eye 7000 A) under D65 light and 10 ° observer.

K/S corresponds to the Kubelka-Munk equation, which is as follows:

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

where K = absorption coefficient, R = reflectance, and S = scattering coefficient.

Assessment of fastness of dyed fabric

ISO105-X12:200, ISO 105-C06 and ISO 105 BO2 standards were employed to measure the rubbing, washing, and lightfastness of dyed samples, respectively.[32]

Measurement of functional properties of dyed samples

To assess the mosquito repellent action of the dyed samples, the "arm in cage" method was used.[33] The standard method of AS/NZS 4399:1996 was utilised to obtain UV protection activity of dyed fabrics.[34] The antibacterial action of dyed fabrics was evaluated using an international method AATCC 100-2004.[35]

Table 1
Combinations of CPBC and ethyl anthranilate used for sample preparation

Sample number	CPBC concentration (%, owf)	Diazotised ethyl anthranilate concentration (%, owf)
1	5	1
2	10	2
3	15	3
4	20	4
5	25	5

Characterisation of dyed fabric

The thermal stability of fabrics (undyed and dyed) was determined by utilising thermogravimetric analysis (TGA) at a heating rate of 20 °C/min and 50-800 °C. XRD (X-ray diffraction) analysis was utilised to evaluate crystalline changes in cotton fabrics after dyeing.

UV-vis spectroscopy of CPBCE

UV-vis spectra of the ethanolic extract of CPBC were recorded using a UV spectrophotometer (UV-1900i, Shimadzu).

Evaluation of physical properties of fabrics

The tensile strength of the fabrics was determined using ASTM D 5035 (1995). The bending length of the fabric was calculated as per ASTMD 1388(1996).

RESULTS AND DISCUSSION

Colour measurement and fastness

Table 2 summarises the results of colour values and the colour strength of dyed samples. Lightness (L*) values got gradually reduced with an increased shade (%), which confirms the increase in shade darkness. The other parameters (a*, b*, and c* values) showed an increment with increasing the concentration of components of the developed shade. The positive values of a* and b* indicate a reddish-yellow shade of dyed samples, and different concentrations of CPBC and ethyl anthranilate resulted in brown shades. The colour strength (K/S) also showed an increment with increasing CPBC and ethyl anthranilate concentrations on cotton, confirming the presence of a higher amount of dye on the fabric.

Table 3 shows the fastness results for the dyed samples. Washing fastness of 4-5, dry rubbing fastness of 4-5, and wet rubbing fastness of 3-4 were obtained. Satisfactory lightfastness properties were also shown by the dyed fabrics. Thus, good dye–fibre interaction is also confirmed through fastness outcomes.

Possible mechanism of azoic dye formation

Figure 1 shows the possible reactions of azoic dye formation using ethyl anthranilate and CPBC. CPBC contains phenolic compounds, such as scopoletin and gallic acid,[23] which react with the diazotised base at para- and ortho- positions adjacent to OH groups. These compounds are water-insoluble. The precipitation of CPBC was observed when it reacted with diazotised ethyl anthranilate, suggesting the water-insoluble nature of the developed azoic dye. The reaction sites and expected structures are shown in Figure 1. The azoic dyes are entrapped inside the fibre matrix, due to which it showed good fixation.

UV-vis spectroscopy of CPBCE

The UV-visible spectrum of the extract showed two peaks of maximum absorbance at 207 nm and 281 nm (Fig. 2). These peaks indicate the presence of various polyphenolic compounds in the extract. The broad peak in the spectrum also suggests the UV protection ability of this extract. The presence of these peaks, as well as the strong UV absorption ability, suggests that the dye absorbs UV rays, which is conducive to the assumption that dyed fabrics would provide UV protection due to the UV absorbing ability of the dye.

Table 2
Colour values, colour strength and developed shades of dyed samples

S. No.	Color values				Color strength	Developed shades
	L*	a*	b*	C*	K/S	
1	78.800	1.945	13.495	13.634	0.473	#1
2	76.956	2.814	16.271	16.513	0.633	#2
3	75.056	4.547	21.107	21.591	0.904	#3
4	72.019	7.182	24.418	25.452	1.259	#4
5	69.593	8.621	26.117	27.503	1.547	#5

Table 3
Fastness results of dyed samples

S. No.	Washing fastness	Rubbing fastness		Lightfastness
		Dry	Wet	
1	4-5	4-5	3-4	4
2	4-5	4-5	3-4	4-5
3	4-5	4-5	3-4	4-5
4	4-5	4-5	3-4	4-5
5	4-5	4-5	3-4	5

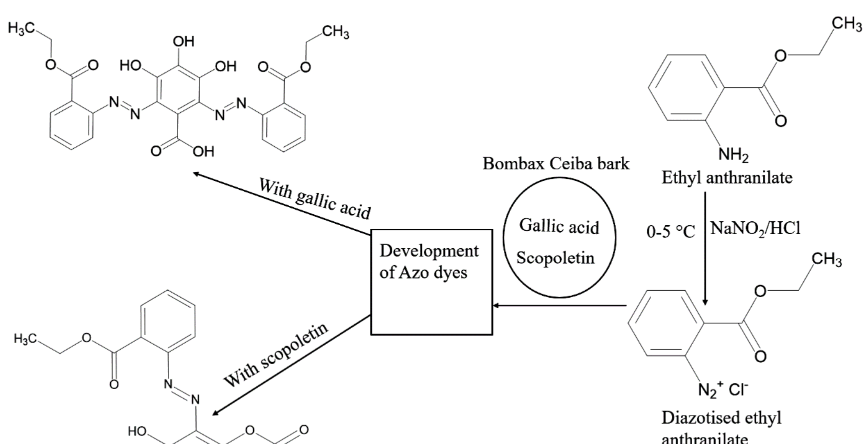

Figure 1: Mechanism of azoic dye formation

Functional effects imparted to dyed fabrics

Table 4 shows the mosquito repellency (%) of dyed samples (1 and 2); all samples offer 100% mosquito repellency. It indicates that the combination of ethyl anthranilate and CPBC at much lower concentrations was sufficient to impart excellent mosquito repellency. The mosquito repellency of 100% was obtained on further increasing ethyl anthranilate concentration. Thus, the fabric dyed with the developed azoic dye was proved as a mosquito repellent substrate.

The data regarding the antibacterial activity of dyed samples are listed in Table 4. Bacterial colony reduction of more than 82% was obtained. The antibacterial activity of dyed fabrics is explained by the presence of phenolic compounds in the dye. Various mechanisms are involved in the bacterial reduction potential of the developed dye. The permeability of the bacterial surface and hydrophobicity were also caused by the presence of gallic acid.[33]

The comparative UPF (UV protection factor) values of undyed and dyed fabrics were evaluated and are shown in Table 5. The UPF values got improved after dyeing. Poor UPF rating was recorded for the undyed cotton, whereas Sample 1 showed a UPF value of 32.02, which lies in the "very good" range. It is evident from the data in Table 5 that, on increasing the concentrations of ethyl anthranilate and CPBC, the UPF values of dyed samples increase. This trend can be explained by the fact that the presence of polyphenols-containing azo dye on the fabric surface contributed to the enhancement of UV protection. Thus, a UV protection ability has been imparted to the dyed fabrics.

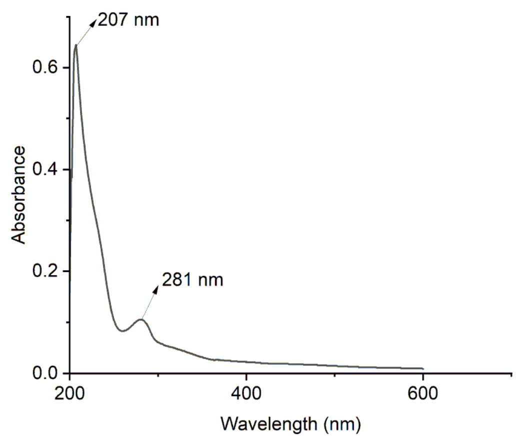

Figure 2: UV-vis spectrum of CPBCE

Table 4
Antibacterial activity and mosquito repellency of dyed samples

Sample	Antibacterial activity (%)		Mosquito repellency (%)
	Staphylococcus aureus	*Escherichia coli*	
1	82.65	85.47	100
2	87.76	89.55	100

Table 5
UPF values of dyed samples

Sample	UPF	Rating
Undyed cotton	8.96 ± 0.40	Poor
1	32.02 ± 7.22	Very good
2	40.75 ± 7.97	Excellent

Characterisation of dyed fabrics

XRD analysis of the dyed and undyed cotton (Fig. 3) samples was performed to analyse the crystal structure and any changes in crystallinity that might occur after dyeing. The peaks observed in cotton samples were located at 15.11°, 16.93°, 23.09°, and 34.81°. A slight reduction in peak intensity was observed in the XRD pattern of the dyed sample. This indicates a decrease in crystallinity after dyeing and confirms a slight distortion of the crystal structure in the dyed sample, which may be caused by the dyeing operation and the dye.

Thermogravimetric analysis (TGA) of the dyed and undyed cotton samples was performed (Fig. 4) under N_2 atmosphere to determine the thermal stability of the samples at a heating rate of 20 °C/min. A slight initial weight loss occurring in both samples was due to the removal of moisture from the fabric. The substantial weight loss in the range of 300-400 °C was caused by the pyrolysis of cotton. The slightly lower weight loss of the dyed fabric is due to the presence of the aromatic ring-based structure of the dye.

Mechanical properties of dyed fabric

Undyed and dyed cotton samples (sample 5) were evaluated for their mechanical properties, namely, tensile strength and bending length. Undyed fabric showed a tensile strength of 652 N, whereas the dyed cotton (sample 5) showed a tensile strength of 540 N. The tensile strength was marginally reduced after the dyeing operation; however, it was still in the acceptable range for dyed cotton. Naphtholation of cotton was carried out under alkaline conditions, which can accelerate the hydrolysis of the cellulose backbone, as well as the formation of oxycellulose. The fabric also became slightly stiffer after dyeing. Thus, this might have resulted in the reduction of the tensile strength of the fabric.

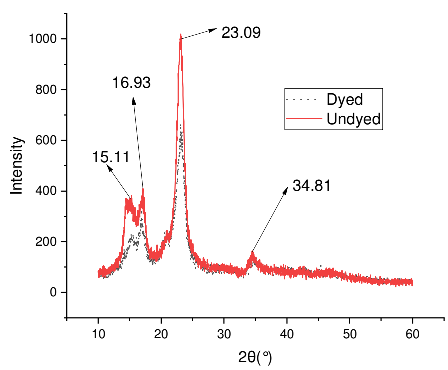

Figure 3: XRD pattern of dyed and undyed cotton samples

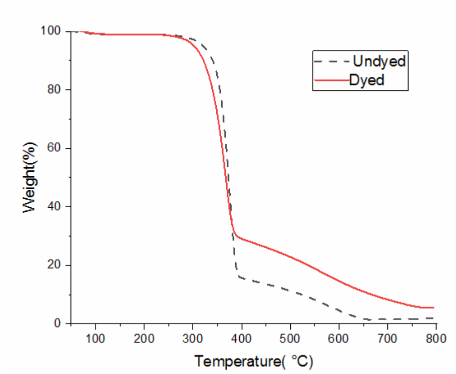

Figure 4: TGA curves of dyed and undyed cotton samples

The bending length of the undyed cotton in warp and weft directions was recorded as 2.6 cm and 2.4 cm, respectively. At the same time, the dyed sample showed bending lengths of 3.4 (warp) and 3.1 cm (weft). This suggests a slight increase in stiffness after azoic dyeing.

CONCLUSION

The cotton fabric was successfully dyed using various concentrations of CPBC and ethyl anthranilate. The mosquito repellent properties were successfully imparted to cotton fabric using sustainable and eco-friendly constituents. The dyed samples showed 100% mosquito repellent properties. The fastness properties and colour values indicated successful dyeing and suggested a good combination of CPBC and ethyl anthranilate as a sustainable option. The UPF values of the dyed samples were found to lie in the "very good–excellent" range. The fabrics were additionally analysed for their mechanical properties. Hence, an innovative method is proposed for dyeing and functional finishing of cotton fabric.

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