CHEMICAL MODIFICATION OF ANCIENT NATURAL DYE FOR TEXTILE BULK DYEING

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ABSTRACT

Increasing demand for Natural dyes is evident due to the environmental concerns opening door for exploitation of various sources. In the present study, an attempt is made to dye polyester fabric with ancient source of natural dye, which has never been used for bulk scale dyeing of textiles so far due to generic draw backs such as low tinctorial capacity and performance properties. Chemical modification can overcome these inherent challenges of natural dye. The chemical modification is carried out by coupling natural dye with diazonium salts of primary amines to get natural source based azo dyes. Three different primary amines namely p- nitro aniline, p-amino phenol and aniline are used. The FT-IR spectra for these dyes indicates the presence of azo group around 1450 to 1520 cm^{-1}.These dyes were then applied on polyester fabrics in aqueous medium which produces brilliant shades with good fastness properties such as wash fastness, rubbing fastness, light fastness and sublimation fastness. The dyed fabrics also showed very good Ultraviolet Protection Factor.

KEYWORDS: Natural Dyes, Azo Dyes, Coupling, Ultraviolet Protection Factor (UPF), Bulk dyeing.

Colouration has been an ancient art. People have added colour to cloth for thousands of years. The coloration of textile fibres is carried out for the purpose of value addition, look and desire of the customer. Anciently coloration of textile was done by dye obtained from the natural sources. In that era the onus of textile coloration was completely fulfilled by natural dyes [Ado et. al., 2014], [Samanta and Konar]. However, natural dyes have some inherent limitations such as poor tinctorial strength, lack of reproducibility, inferior fastness properties and unexhausted mordant in the residual dye bath which may pose serious effluent disposal problem. Due to these limitations and after the invention of first artificial dye in 1857 the textile industry has turned to synthetic dyes. Natural dyes lost their significance since the advent of synthetic dyes [Morris and Travis, 1992], [Krani and Goodarzian, 2010].

However, due to the stringent environmental standards imposed by many countries in response to the hazardous effluent generated during synthesis and toxic and allergic reactions associated with the synthetic dyes, the textile researchers have once again being enthralled by natural dyes.Today, many are rediscovering the joy of achieving colour through the use of renewable, non-toxic, natural sources [Nimkar and Bhajekar, 2006], [Deo and Desai, 2006].

Textile printing is the most versatile and important of the methods used for introducing colour and design to textile fabrics. It is probably the cheapest method of ornamenting textile materials and is very popular because of the beautiful effects produced by it. Kalamkari is an ancient painting method. The word ‘Kalamkari’ is derived from two Hindi words ‘Kalam’ and ‘Kari’ (or Karigari), ‘Kalam’ meaning pen and ‘Kari’ meaning art. Kalamkari printing as such painting, therefore, means printing carried out by hand by means of a pen. This ancient painting method used natural colours for painting. One of the important natural colours used is Kasim Kaaram, black colour, which is used to draw design outline [Gächter and Paramparik, 2009]. This dye, in this research have been studied for its application in textile dyeing.

The dyeing of polyester is difficult as it is a hydrophobic fibre it does not swells in water because of its compact structure. In the present study, an attempt is made to dye 100% polyester fabric with an ancient source of natural dye (Kasim Kaaram). This ancient source of natural dye is chemically modified by coupling it with diazonium salts of three different primary amines to modify its substantivity and tinctorial capacity to overcome inherent limitations of natural dyes.

MATERIALS AND METHODS

Materials

Source:Kasim Kaaram(Ancient natural dye)

Substrate used: Industrially ready for dyeing (RFD) 100% polyester fabric was purchased from local manufacturer in Mumbai.

Chemicals used: p- nitro aniline, p-amino phenol and aniline, sulphuric acid, hydrochloric acid, sodium nitrite, N, N-dimethyl formamide and acetone were supplied by SD fine chemical ltd. (Mumbai, India).

Methods

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In this work we have chemically modified the Kasim Kaaramby coupling it with diazonium salts of three different primary aminesnamely p- nitro aniline, p-amino phenol and aniline. These amines are firstly diazotized to form theirdiazonium salt which is then coupled with Kasim Kaaramto form the natural source based azo dyes.

EXPERIMENTAL

Preparation of Kasim Kaaram (ancient natural Black)

Natural black is prepared by soaking cane jaggery, iron fillings and water in a ceramic pot for fifteen days. Cane jaggery was allowed to dissolve in water, after which iron fillings were added. The solution was stirred once in a few days and covered immediately. The fermentation takes place in a closed pot. The reaction takes place between molasses and the iron fillings to form the resultant solution, which is further used as a coupler.

Diazotisation of p-nitro aniline

1.25 gm. of p- nitro aniline was dissolved in 2.0 ml of concentrated sulphuric acid. 10g of ice and 10 ml of distilled water was mixed with dissolved solution and stirred vigorously while being cooled to 0-5^0 C. Most of the p- nitro aniline gets dissolved. A solution of 0.63g $NaNO_2$ dissolved in 5ml distilled water was added drop wise to the reaction mixture while maintaining the temperature of the reaction 0-5^0 C. It gave a solution of diazonium salt solution based on p-nitro aniline.

Diazotisation of p-amino phenol

1.20 g of p-amino phenolwas dissolvedslowly in 12 ml of concentrated hydrochloric acidby continuous stirring and was further diluted using distilled water until the p-amino phenol is dissolved completely. The p-amino phenol solution was cooled to 0-5^0 C in ice bath. Pre-dissolved 0.70 g sodium nitrite was added to the reaction mixture, while continuous stirring. Thus diazonium salt solution based on p-amino phenol was formed.

Diazotization of aniline

0.2 g of aniline was dissolved in a mixture of 1 ml of distilled water and 10 ml of concentrated hydrochloric acid. The solution was kept in an ice water bath. 1 ml of 10% sodium nitrite solution was added to reaction mixture and the temperature of reaction bath was maintained between 0-5^{0}C.Thusdiazonium salt solution based on aniline was formed.

COUPLING

The 0.5 g of ancient natural dye was dissolved in 2 N Sodium hydroxide solution with constant stirring. This solution is used as a coupling component. For the synthesis of modified natural dyes, the respective diazonium salt solutions were added drop wise to mixture of coupling component which is further stirred for 2-3 hours in ice bath. This dyes were then filtrated on Buchner funnel using suction filtration, washed with cold water and dried at 60^{0}C in oven.

Application of modified natural dyes

Synthesized natural source based azo dyes were then applied on industrially ready for dyeing 100% polyester fabric in aqueous medium. Dyeingof polyester was carried out in high temperature high pressure (HTHP)

Dyeing machine at 130^{0}C for 45 minutes by keeping material to liquor (MLR) ratio 1:30. Further dyed fabric was subjected to reduction clearing and washing. Shades obtained were then evaluated for their fastness properties such as wash fastness, rubbing fastness, light fastness and sublimation fastness.

COLOUR MEASUREMENTS

Dyed fabrics were simultaneously evaluated in terms of CIELAB colour space (L*, a* and b*) values and colour strength in terms of K/S. In general, the higher the K/S value, the higher the depth of the colour on the fabric. L* corresponding to the brightness (100 represent white, 0 represents black), a* corresponding to the red-green coordinate (+ve represents red, -ve represents green) and b* corresponding to the yellow–blue coordinate (+ve represents yellow, -ve represents blue). As a whole, a combination of all these enables one to understand the tonal variations. Four locations on the dyed fabric were arbitrarily chosen and L*, a* and b* values were measured by spectrophotometer. The CIE L*a*b* colour difference between any two points was calculated. The levelling properties of the dyes on polyester fabric were assessed using the mean of five such colour difference results (Lee et al., 2005).

The dyed samples were evaluated for the depth of colour by reflectance method using 10^0 standard observer. The absorbance of the dyed samples was measured on Rayscan-Spectrascan 5100+ equipped with reflectance accessories. The K/S values were determined using expression;

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

Where, R is the reflectance at complete opacity; K is the Absorption coefficient & S is the Scattering coefficient.

COLOUR FASTNESS TESTING

Colour fastness to washing (ISO 105 C03)

The dyed fabric specimens of size 10×4 cm were placed between two pieces of undyed cotton and wool fabric measuring 5×4 cm, these three pieces were held together by stitching around edges leaving 5×4 cm area exposed. Specimens were washed in lauder-o-meter at 60^0C, for 30minutes in wash liquor containing5gpl soap solution and 2 gpl soda ash. After washing, specimens are unstitched, dried and colour change of dyed sample and staining on undyed samples is assessed using grey scale. (Rating 1–5, where 1-poor, 2 -fair, 3-good, 4-very good and 5-excellent).

Colour fastness to rubbing (ISO 105 X12)

A strip of dyed specimen (12×60 cm) is mounted on the crock meter. A white cotton fabric piece (5sq cm) of undyed cloth is clamped on the wooden finger of the rubbing device of the instrument and rubbed to and fro 10 times against the specimen. The colour transferred from dyed fabric to white fabric is then assessed by comparing with the grey scale. For wet rubbing fastness,the undyed fabric is wetted with water, squeezed off and then clamped on the finger. (Rating 1-5, where 1-poor, 2-fair, 3-good, 4-very good and 5-excellent)

Colour fastness to light (AATCC standard)

Dyed fabric specimensto be tested were mounted in a light fastness chamber such that half of the dyed specimen get exposed to light. After mounting samples, the standard lamp is switched on and kept for 18 hrs. The samples were compare with a standard blue wool scale.(Ratings, 1-8, where 1-poor, 2 -fair, 3-moderate, 4-good, 5-better, 6-very good, 7-best and 8-excellent).

Colour fastness to sublimation (ISO105 F04)

The dyed specimens to be tested were sandwiched between cotton and polyester white fabrics. These specimen were kept on the plates of sublimation fastness tester which were maintained at different temperatures (150^0C, 180^0C, 210^0C) for 30 seconds, and subsequently evaluated for change in colour and staining of the adjacent fabrics by comparing with grey scale.(Rating 1-5, where 1-poor, 2-fair, 3-good, 4-very good and 5-excellent)

RESULTS AND DISCUSSION

Components and percentage yield of the modified natural dyes

Dye, coupling component, type of diazonium salt, percentage yield, hue and solubility of the natural source based azo dyes are given in table I.

Table I: Dye, coupling component, type of diazonium salt, percentage yield, hue and solubility of modified natural dye

Dye	Coupling component	Type of diazo nium salt	% yield	Hue	Solubility
NA1	Ancient natural dye	p-nitro aniline	88	Greenish black	Acetone/ DMF
NA2	Ancient natural dye	p-amino phenol	70	Black	Acetone/ DMF
NA3	Ancient natural dye	Aniline	85	Blackish brown	Acetone/ DMF

Table II: Colour values in terms of K/S and CIE L*a*b* values

	CIE L*a*b* values			
Dye	L^*	a^*	b^*	K/S
NA1	49.09	9.05	31.09	5.13
NA2	36.70	6.12	16.91	1.55
NA3	46.76	7.56	30.84	11.59

The colour data as shown in table II are in agreement with the spectral data of the all the three modified natural dyes. As K/S values is higher in case of NA3 dye (11.59), it gives higher depth on polyester fabric as compare to depth of colour in case of other two dyes. Thus order of depth of shade NA3 >NA1>NA2 and their values were in a positive coordinates in terms of a* (red) and b*(yellow).

FT-IR analysis

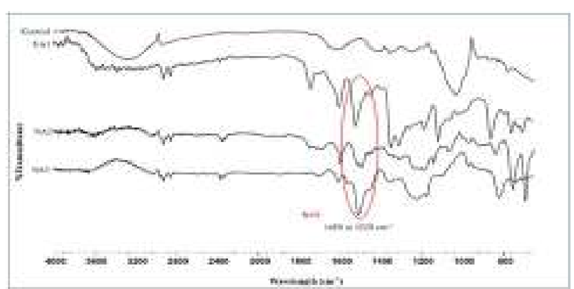

Figure 1: FT-IR spectra for ancient natural source (control sample) and all three modified natural dyes

In Fig.1, the FT-IR spectra for Kasim Kaaram (control sample) showsthe presence of benzene ring in aromatic compounds as indicated by the sharp peak with medium intensity in the range of 1615-1590 cm^{-1}.The presence of C-N stretch in aromatic compounds is indicated with strong intensity peak in the range of 1280-1180 cm^{-1}. N-H stretchpeak with medium intensity for the presence of primary, secondary amines and amides is indicated in the range of 3500-3100 cm^{-1}. Thus the FT-IR spectrum for control sample shows the characteristic bands which are amenable for chemical modification. Whereas the FT-IR spectra for all the three modified dyes NA1, NA2, NA3 respectively shows the presence of azo groups in the range of 1450-1520 $cm\text{-}^{1}$which indicates the successful chemical modification of Kasim Kaaram.

Table III: Dye, It's hue on polyester fabric and Dyed samples

Dye	Hue on polyester	Dyed sample
NA1	Bright brown	
NA2	Bright grey	
NA3	Dark brown	

The table III gives data on hues obtained on the polyester fabrics. The dyes gavebright brown, bright grey and dark brown hues on the polyester fabrics respectively for NA1, NA2 and NA3 dyes.

Fastness properties of modified natural dyes

Table IV: Results for Wash, Rubbing and Light Fastness

Dye	Wash fastness		Rubbing fastness		Light fastness
	Change in colour	staining	Dry	Wet	Change in colour
NA1	4	4	5	4	7
NA2	4	4-5	5	4-5	6-7
NA3	3-4	4-5	5	4-5	7

Table V: Results for Sublimation Fastness

Dye	At 150^0C		At 180^0C		At 210^0C	
	A	B	A	B	A	B
NA1	4	4-5	4	4	4	4
NA2	4	5	4	4-5	4	4
NA3	4-5	4-5	4	3	3	3

(A=Change in colour, B=Staining)

The polyester fabrics dyed using the modified natural dyes were subjected to assessment of wash, rubbing, light and sublimation fastness. Results for wash, rubbing and light fastness are summarised in table IV and the results for sublimation fastness are summarised in table V. The results clearly indicate excellent all round fastness properties for all the three modified natural dyes used for dyeing of polyester fabric. Wash fastness obtained was in the range of "very good" to "excellent' scale for both, change in shade of the dyed fabric and staining on white fabric. Also in case of rubbing fastness results are in the range "very good" to "excellent" for both dry rubbing and wet rubbing. Light fastness properties were also found to be excellent for all the dyed fabrics. Also, in case of sublimation fastness for all the three dyes we have got excellent fastness properties.

Ultraviolet Protection Factor (UPF)

Textile Clothing can protect the skin from harmful UV radiations because the fabric can reflect, absorb and scatter these rays and reduce the amount of radiation transmitted through it. UV protection provided by a textile material is measured in terms of its ultraviolet protection factor (UPF). It is defined as a ratio of average effective UV irradiance calculated for unprotected skin to the average UV irradiance calculated for skin protected by the test fabric. Below is the (table VI) classification scheme for UPF rating published in 1996, the Australian and New Zealand standard for evaluation and classification of sun protective clothing (AS/NZ 4399) which is considered the benchmark for industry [Sayed et. al., 2015].

Table VI: Classification scheme for UPF rating

UPF rating	% UVR transmitted	Protection Category
15-24	6.7-4.2	Good
25-39	4.1-2.6	Very Good
40-50+	≤ 2.5	Excellent

Table VII: Results for Ultraviolet Protection Factor (UPF)

Fabric dyed with dye	UPF rating
Undyed PET or control sample	12.10
NA1	30.10
NA2	28.35
NA3	32.12

The results for Ultraviolet Protection Factorgiven in table VII shows that all the three dyed fabrics shows very good UPF rating as UPF is in the range of 25-39 which indicates the transmittance of 4.1-2.6 %(i.e. Blocking 95.9-97.4%) of the UV radiation which imparts the very good ultra violet protection properties to the textile material.

CONCLUSION

Successful chemical modification can be done to overcome the inherent limitations of Kasim Kaaram such as poor tinctorial strength, lack of reproducibility, inferior fastness properties making it suitable for the bulk scale application. Due to modification the requirement of mordant for dyeing is also eliminated with its consequent drawback. All the three modified natural dyes were successfully applied on 100% polyester fabric in an aqueous medium with brilliant shades. Dyed fabrics exhibit excellent overall fastness properties and also found to give very good ultra violet protection factor.

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