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Ecological dyeing of Woolen yarn with *Adhatoda vasica* natural dye in the presence of biomordants as an alternative copartner to metal mordants

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ABSTRACT

Introduction of natural dyes into modern dye houses is very promising green chemistry concept which should be popularized more and more to reduce the dependency of wool dyeing on some toxic and non-biodegradable synthetic dyes (Azo and benzidine dyes). In the present study, an attempt has been made to investigate the possibility of wool dyeing with *Adhatoda vasica* extract as a natural dye. A beautiful color palette of shades of varied hue and tone were obtained by using different mordants. The effect of various metal salts (ferrous sulphate, alum and stannous chloride) and natural tannin extracts (gallnut, pomegranate peel and babool bark) as mordants on color and fastness properties of dyed wool samples was comparatively evaluated. Dyeing experiments were performed with and without mordants, using pre-mordanting technique. The color of dyed woolen yarn was investigated in terms of CIELab (L*, a* and b*) and K/S values; and fastness properties were determined as per ISO and AATCC standard test methods. As confirmed by exhaustion studies, a substantial portion of metal salts remained in residual mordant baths. The results of using biomordants for wool dyeing were comparable with that of the metallic mordants in terms of color strength and fastness characterisctics. Biomordants produced quite different color gamuts as expected from a mordant and thus offer full potential to replace metal salts in wool dyeing.

1. Introduction

A revived interest in the use of natural dyes in textile and food coloration has been growing since last few decades and there is an urgent need for availability of natural dye yielding plants for fulfilling the purpose. Recently discovered properties of natural dyes such as insect repellent [1], deodorizing [2], flame retardant [3], UV protection [4], fluorescence [5,6], and antimicrobial activity [7–9], besides being biocompatible, biodegradable, renewable, and non-toxic have revolutionized all industrial sectors especially textile industry for producing more appealing and highly functional value-added textiles [10,11]. This is a result of ecological concerns related with the use of 118 of the azo and benzidine synthetic dyes with 24 carcinogenic aromatic amines as their primary photolytic degradation products, which have motivated researchers all over the globe to explore new eco-friendly substitutes for minimizing their negative environmental impacts [12]. In the application of natural dyes, different dyeing and mordanting techniques and post-treatment were used to improve color fastness properties. As a result, optimization of the dyeing conditions with regard to the type of natural dye is quite common and a broad set of variations in the dyeing recipes is given in the literature [13,14]. The numerous variations of dyes from plant sources and dyeing processes make an introduction of natural dyeing into full-scale technical dyeing processes rather difficult. The rapid changes in trends, fashion and the demand for good fastness properties on different substrates requires a basic database describing possible applications of natural dyes, otherwise too much parallel optimization work has to be done by each dyehouse.

But intrinsic lower light fastness, poor shade reproducibility, non-standardization of raw material and complexity of process involved in natural dyeing restricts their use in textile applications,

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besides many advancements have been taken into consideration for modifying color characteristics of dyed textile materials [15–17]. Mordants are essential components of natural dyeing processes in terms of achieving broad spectrum of colors of various patterns and special performance characteristics on wide range of natural as well as synthetic textile materials [18–21]. Chemical nature of mordant and fiber-mordant-dye interactions greatly modifies the color characteristics of dyed textile. Most common mordants in natural dyeing used to alter the colorimetric parameters and fastness properties of dyed textile materials are aluminium, potassium dichromate, copper sulphate, ferrous sulphate, and stannous chloride [19]. Use of rare earth metals have been successfully employed as mordants for increasing dyeing performance of ramie fabrics [22]. Although, significant amounts of metal ions remains unexhausted in residual mordant baths which eventually are discharged in waste waters, thereby posses ecological concerns and negative impact on public health [20]. The amount of metal ion discharged from textile industries is strictly banned beyond a certain limit [22–24]. Advancements in mordanting processes and selecting new, safe and ecofriendly mordants to replace traditional heavy metal ions has been an important part in the development of natural dyeing processes [25].

The textile industry is one of the biggest consumers of water, so extensive data about the effluent production have been collected and are available from the literature [15]. Thus, depending on the extent of after treatments relating to the release of effulents produced from dye houses, waste water from the dyeing step is diluted more or less to reduce the load of toxic chemicals. Use of natural mordants (Biomordants) in place of metallic salt mordants has been advised by researchers in terms of an effective and safe alternative considering environmental aspects of pollution and their biodegradable nature, hence can be discharged to the environment without any chemical or physical treatment (e.g. precipptation or filtration) [26–28]. Mordants from natural origin such as myrabolan (*Terminalia chebula*), pomegranate rinds (*Punica granatum*), tannin, tannic acid, tartaric acid, guava and banana leaves ash have been utilized for mordanting purpose [29]. Recently, lot of research finding have been done regarding use of biomordants as an alternative and safe substitute to metal mordants and encouraging results have been achieved [30–33]. Biomordants are biological natural materials having metal ion(s), tannins etc. mostly come from vegetable sources and act as mordant in natural dyeing processes. Some plants and plant parts with high tannin or metal content may present mordanting effect to various extents depending on their chemical structure and amount of metal present in them [34].

In continuation to our earlier studies [35] of thermodynamics and kinetic investigation on wool dyeing with the evaluation of colorimetric and fluorescence characteristics with *A. vasica* natural dye, present study was undertaken in order to investigate dyeing properties of *A. vasica* dye alone (Control dyeing) and in conjunction with small amounts of metal mordants and alternative biomordants. Additionally, comparison between metal mordanted and biomordanted woolen yarn samples were also done with the aim of making this research a viable alternative for non-biodegradable metal mordants with ecofriendly, biodegradable and nontoxic biomordants.

2. Materials and methods

2.1. Materials

100% pure New Zealand Semi worsted woolen yarn (60 counts) was procured from MAMB Woolens Ltd. Bhadohi, S R Nagar Bhadohi (U.P.), India. Powdered *Adhatoda vasica* leaves extract and biomordants (extract of gallnut, pomegranate rind and babool) were purchased from Sir Biotech India Ltd. Kanpur (U.P.), India. Metallic mordants iron II sulphate, alum and tin II chloride used were of laboratory grade. Sodium acetate and sodium hydrogen carbonate buffer were purchased from Merck.

2.1.1. Dye component

Adhatoda vasica (L.) Nees (Family Acanthaceae), a well known shrub found throughout Indian peninsula up to an altitude of 1300 m, possesses an imperative place in Ayurvedic and Unani medicine for the treatment of various diseases and disorders, particularly respiratory tract ailments [36]. It is a fast growing plant with unknown (unreported) annual production but coppices well. The main chemical component present in *A. vasica* is a bitter quinazoline alkaloid Vasicine in addition to vasicinone, vasicinol, adhatodine, adhatonine, adhavasinone, anisotine, and peganine [37,38]. It is well known that *Adhatoda vasica* contains 2-pyridyl methyl amine and gives yellow color with alum, light yellow with copper sulfate and gray with ferrous sulfate [39]. Besides possessing varied and high therapeutic potential researchers have tried to explore dyeing properties of *A. vasica* and introduce it in textile industry as a potential finishing agent. However, very little information is available related its dyeing potential [35,39].

2.1.2. Biomordants

Quercus infectoria (Gallnut/Aleppo oak) belongs to family Fagaceae is indigenous to Greece, Asia Minor, Syria, and Iran. The galls of *Q. infectoria* contain mixture of gallotannins, gallic acid, and ellagic acid as principal constituents (50–70%) and find extensive application in tanning, mordanting, dyeing, and manufacturing of ink. The main coloring component in gallnut extract is ellagic acid, which has an affinity for dyeing substrates due to the presence of −OH (auxochrome group) [8,40].

Ellagic acid is the main coloring component of pomegranate rind (PPE) [41]. Pomegranate juice contains various types of anthocyanins mainly cyanidin-3-glucoside, delphinidin-3-glucoside, pelargonidin-3,5-diglucoside, cyanidin-3,5-diglucoside, delphinidin-3,5-diglucoside and pelargonidin-3-glucoside. The outer covering of pomegranate has been known to be very rich in ellagitannins and gallotannins [42,43].

Babool (*A. nilotica*) is a rich source of polyphenols, mainly composed of condensed tannin and phlobatannin in addition to gallic acid, ellagic acid, (+) − catechin, and (−) − epigallocatechin-7-gallate [44,45]. Bark of babool constitutes one of the most important tanning materials of Northern India; tannin content varies from 9 to 16.5% on dry weight basis [46]. Tannin content present in *A. nilotica* can be explored as an effective biomordant for the production and development of environment friendly textile materials [47,48].

2.1.3. Instruments

A Perkin Elmer Lambda-40 double-beam UV–visible spectrophotometer was employed for recording absorbances values of dye bath solutions. A pH/mV Meter (BD 1011) from Decibel digital technologies was used for measuring pH of dye solutions.

2.2. Methods

2.2.1. Mordanting

Woolen yarn samples were mordanted by pre-mordanting technique using 10% (o.w.f.) potassium aluminium sulfate ($K_2Al_2(SO_4)_4.24H_2O$), 5% (o.w.f) ferrous sulfate ($FeSO_4.5\%H_2O$), 1% (o.w.f.) stannous chloride ($SnCl_2{\cdot}2H_2O$) and 1–5% (o.w.f.) biomordants namely gallnut, PPE and babool. Before the application of mordants, woolen yarns samples were soaked in non-ionic detergent solution (5 ml/L) to increase surface wetability.

Mordanting was done for 45 min with material to liquor (M:L) ratio of 1:50 at 90 °C. Mordanted woolen yarn samples were thoroughly rinsed with tap water to remove superfluous (unused) mordants.

2.2.2. Dyeing

Dyeing experiments were performed using separate conventional baths with M:L ratio of 1:50 for 20% (o.w.f.) *A. vasica* dyeing at 90 °C for 60 min. In order to get uniform dyeing, samples were manually stirred regularly (after every 5 min). Control dyeing was also done in the concentration range of 1–20% (o.w.f.) in order to access the effect of dye concentration on color strength and colorimetric properties of dyed woolen yarn. Finally, dyed samples were treated with 5 ml/L non-ionic detergent (Safewash Wipro), rinsed with tap water and dried in shade.

2.2.3. Effect of pH on the adsorption of A. vasica *extract onto woolen yarn*

Woolen yarn samples were treated with 20% (o.w.f.) of *A. vasica* extract at 90 °C for 60 min. The treatment solution was adjusted in the pH range of 2–9 by means of sodium acetate and sodium hydrogen carbonate buffer solutions. The percentage exhaustion/dye uptake (amount of dye adsorbed onto woolen yarn) of *A. vasica* dye on woolen yarn at different pH values was calculated as follows:

$$\%\ Exhaustion = \frac{A_0 - A_1}{A_0} X100 \quad (1)$$

Where, A_o and A_1 are the absorbance at λ_{max} 271 nm before dyeing and after dyeing respectively.

2.2.4. FT-IR spectroscopic investigation

FT-IR spectra of woolen yarn before and after application of metal salts and dye were obtained on "Perkin Elmer Spectrum RXI FT-IR System" in order to investigate and observe fibre-mordant-dye interactions (with the resolution of 2 cm^{-1}). Discs were prepared by cutting samples into fine pieces and grinded with KBr, used as internal standard. Amide I, II and III bands in the FT-IR spectra were resolved in accordance with literature data.

2.2.5. Color measurement

The colorimetric properties of dyed woolen yarn samples were obtained using Hunterlab XE plus Color scan under illuminant D65 using 10° standard observer in terms of CIELab and CIELch values (L*, a*, b*, c*, h°) and color strength (K/S). The color strength (K/S) in visible region of spectrum (400–700) nm was calculated based on Kubelka-Munk equation:

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

Where, (K) is adsorption coefficient, (R) is reflectance of dyed sample and (S) is scattering coefficient.

The Chroma (c*) and hue angle (h°) were measured by using following equations:

$$Chroma(c*) = \sqrt{a^2 + b^2} \quad (3)$$

$$Hue\ angle(h^\circ) = tan^{-1}\left(\frac{b}{a}\right) \quad (4)$$

2.2.6. Fastness testing

The light fastness of dyed woolen yarn samples were measured by Digi LIGHT-Nx™, as per test method ISO 105-B02:1994 (Amd.2:2000). The wash fastness of dyed woolen yarn samples were measured by Digi WASH-SS™ (Launderometer) as per ISO 105-C06:1994 (2010) specifications. Dry and wet rub (crocking) fastness of dyed woolen yarn samples were tested using a Digi CROCK™ (Crockmeter) as per ISO 105/X12:2001 by putting the fabric on panel and giving ten strokes for both dry and wet rub (crocking) fastness tests. The samples were also assessed for staining on white cotton and adjacent wool fabrics.

3. Results and discussion

3.1. Evaluation of effect of pH on the adsorption of A. vasica *dye extract*

Generally pH of dye solution is one of the most important parameter controlling dye adsorption. Fig. 1 reflects the variation of dye exhaustion (amount of dye adsorbed onto woolen yarn) as function of different pH values with initial dye concentration of 20% (o.w.f) at 90 °C for 60 min having M:L ratio of 1:50 for control dyeing (without mordanting). An increasing trend in percentage exhaustion have been observed with decreasing pH over the range of 3–9 but dropped down at pH lower than 3. The maximum dye exhaustion was observed in the pH range of 2–4. This is mainly due to increase in the protonation of amino groups of wool under acidic conditions, which is beneficial for ion-dipole interactions with hydroxyl group of vasicine. Additionally, hydroxyl groups of vasicine can form hydrogen bonding with amine groups of wool fiber [35]. The percentage dye exhaustion at pH 7 dropped to 26.08, showing weak electrostatic interactions between wool and dye components in neutral pH conditions.

3.2. FT-IR analysis of wool-mordant-dye interaction

FT-IR spectra of wool fiber, mordanted wool fiber and mordanted dyed wool fiber are presented in Fig. 2. Infrared spectra of wool fiber (Fig. 2a) indicate characteristic absorption peaks assigned mainly to peptide bond which represents the fundamental structural unit of the polypeptide chain [6,9]. The atoms in peptide bond oscillate; giving rise to IR spectral bands determined as I, II, and III amide bands [49]. The NH stretching and bending vibration related to amide I vibration appears at 3280 cm^{-1} and 1640 cm^{-1}, respectively. The C=O stretching vibration band, appears in the region between 1630 and 1670 cm^{-1}, probably overlapped with amide I vibration (N—H bending) [50]. All characteristics peaks of wool fiber were found in the mordanted samples with low intensities. Shifts observed with

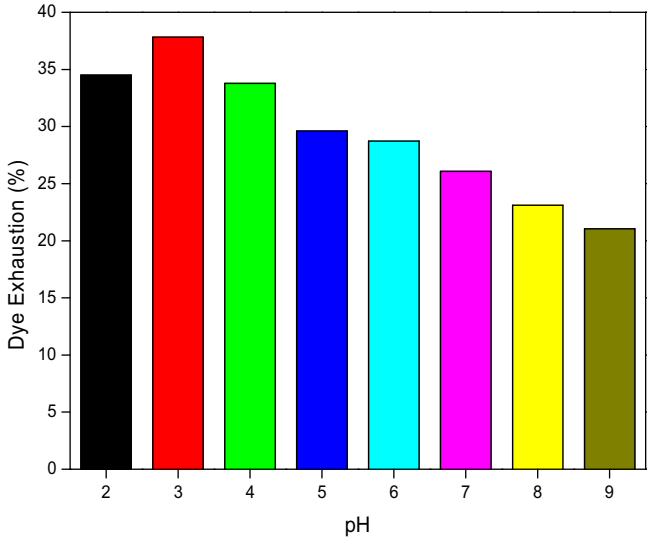

Fig. 1. Effect of pH on the adsorption capacity of *A. vasica* onto woolen yarn.

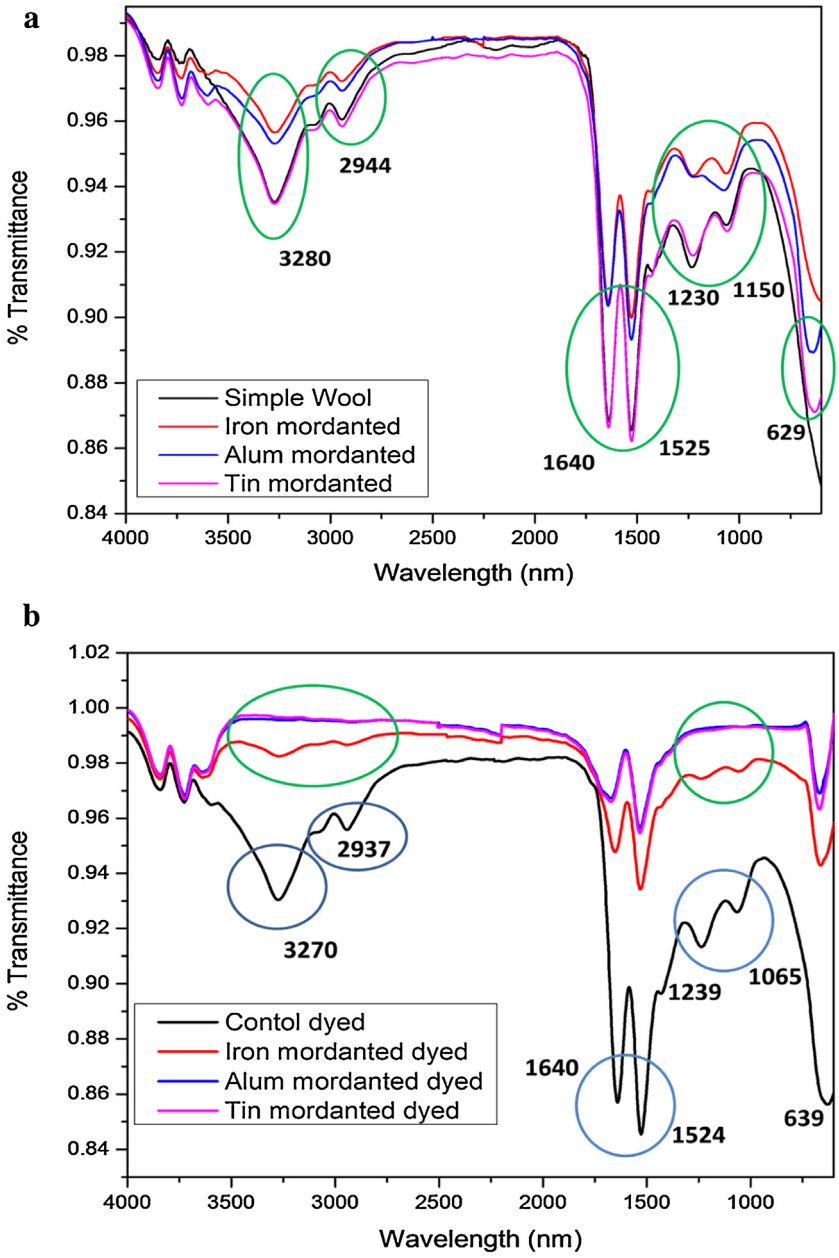

Fig. 2. FT-IR spectra of; (10a) mordanted woolen yarn, and (10b) dyed woolen yarn.

Table 1
Percentage metal and dye exhaustion.

Metal mordants	Percentage Metal exhaustion	Metal ion conc. in residual mordant both
5% (1 g/L) Ferrous sulphate	73.77	0.53 g/L
10% (2 g/L) Alum	63.31	0.73 g/L
1% (0.2 g/L) Stannous Chloride	69.19	0.052 g/L

Dye (*A. vasica*)	Mordants	Percentage dye exhaustion
20% (o.w.f.)	Un-mordanted (Control)	37.97
	5% Ferrous sulphate	58.42
	10% Alum	38.83
	1% Stannous chloride	49.33
	5% Gallnut	52.23
	5% PPE	48.19
	5% Babool	42.27

amide III (1230 cm^{-1}) and CN stretch of amide III band (1150 cm^{-1}) in samples treated with ferrous sulfate, alum, and stannous chloride confirms successful complex formation among metal ions and wool fiber.

Fig. 2b, shows the FT-IR spectra of dyed wool fibers. Intensity and shifting of peaks relating to C—N stretching frequency of amide I and amide III bands of dyed wool fiber at 3270 cm^{-1}, 1239 cm^{-1}, and 1065 cm^{-1} indicates the involvement of amine groups in the interaction between fiber, mordant and dye molecules.

3.3. Environmental impact of dyeing waste water

Nearly all-natural dyes with a few exceptions require mordants to fix them onto textile materials. While mordanting and dyeing processes, substantial portions of metal mordant remains unexhausted in the residual dye bath and may pose serious effluent disposal and environmental related problems [15,20,51]. From the results, it is clear that amounts of metal ions that remain unexhausted in the mordant baths is more than the legal limits for textile effulents [15]. The amounts of metal ions in residual mordant baths were found to be highest for ferrous sulphate 0.53 g/l out of 1 g/l (53%) followed by alum 0.73 g/l out of 2 g/l (36.5%) and stannous chloride 0.052 g/l out of 0.2 g/l (26%), and depending upon the concentrations used (Table 1).

3.4. Evaluations of dye exhaustion

The amount of dye uptake by woolen yarn for both mordanted as well as unmordanted samples was expressed in terms of percentage dye exhaustion (Table 1). Mordanting increased dye exhaustion to a significant extent. Among the metal mordanted samples maximum exhaustion was observed in case of ferrous sulphate followed by stannous chloride, alum, and unmordanted samples. The differences in exhaustion rates were due to the differences in fiber-mordant-dye interactions. It was shown that use of iron slats resulted in the formation of 1:2 metal-dye complexes within dyed substrate which eventually increases dye exhaustion on account of higher coordination compound formation ability [52,53] as compared to alum and stannous chloride. Higher amounts of tannins present in gallnut extract accounts for its maximum exhaustion rate followed by PPE and babool [8,54].

3.5. Colour measurement evaluation

3.5.1. Control dyeing with Adhatoda vasica

The color measurement values (CIEL*a*b* and K/S) of unmordanted woolen yarn dyed with *A. vasica* in the concentration range of 1–20% are given in Table 2 and Fig. 3. It is clearly evident from Fig. 3 that color strength values increased with the increase in the concentration of the dye with highest K/S value of 4.01 observed for 20% dye concentration. The force responsible for dye transfer from dye bath to fibre is function of concentration gradient of dye in two phases (solution and fibre). Extent of dye transfer from solution to woolen yarn enhanced with increase in dye bath concentration, and thus apparent depth of shades also increased.

Table 2
CIEL*a*b* values for control dyed samples.

S.No.	*A. vasica*	L*	a*	b*	C*	h°
C_1	20%	61.09	5.89	18.20	19.13	72.06
C_2	15%	61.51	5.60	17.82	18.68	72.54
C_3	10%	61.70	4.39	16.24	16.82	74.87
C_4	8%	62.04	4.20	16.19	16.72	75.43
C_5	5%	64.64	3.68	16.15	16.56	77.16
C_6	3%	65.22	3.44	15.91	16.28	77.80
C_7	1%	69.70	2.46	15.84	16.03	81.17

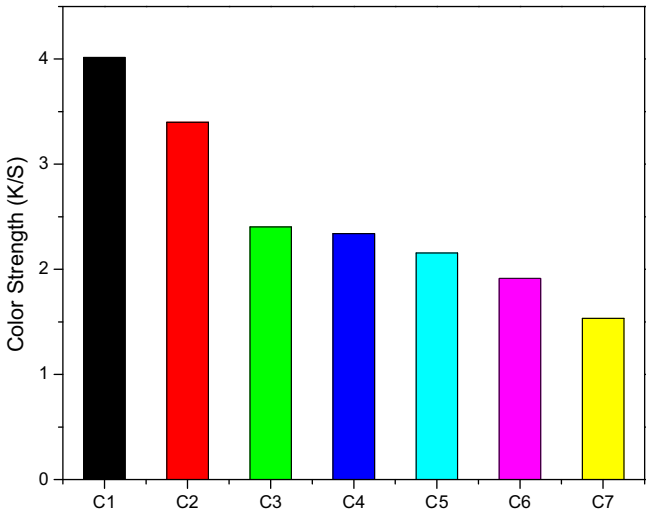

Fig. 3. Color strength (K/S) of woolen yarn dyed with *A. vasica* natural dye.

Application of *A. vasica* dye onto woolen yarn produced light and bright shades showing high lightness (L*) and low chroma (c*) values with hue angle ranging from 72° to 82°. The concentration of natural colorant in the dye bath also effected the lightness values of dyed woolen yarn, high lightness values were observed at low concentrations of dye. From a*-b* values, it is evident that samples dyed with low concentrations of *A. vasica* are shifted towards yellow region of red-yellow coordinate of CIELab color space with light, bright and less saturated shades.

3.5.2. Color evaluations of metal mordanted woolen yarn

As mentioned earlier, the role of the mordant is to secure a dramatic improvement in both the fastness properties of the dyed samples to light and wet agencies via the formation of a stable coordination complex with the metal ion in situ within the wool fibre, this being accompanied by a marked change in the colour of the dyed samples. Often the colour of the dye on woolen yarn/fiber

Table 3
CIEL*a*b* values for mordanted dyed woolen yarn samples.

S.No.	Mordants	*A. vasica*	L*	a*	b*	C*	h°
C_1	Control	20% (o.w.f)	61.09	5.89	18.20	19.13	72.06
	Metal Mordants						
M_1	Iron		47.21	7.26	16.93	18.42	66.77
M_2	Alum		61.75	5.13	19.96	20.61	75.58
M_3	Tin		53.46	7.75	19.43	20.92	68.27
	Bio-mordants						
	Gallnut						
G_1	1%		51.01	5.61	17.30	18.18	72.03
G_2	2%		50.58	5.74	17.31	18.23	71.65
G_3	3%		51.68	5.26	17.14	17.93	72.93
G_4	4%		52.17	5.49	17.33	18.17	72.41
G_5	5%		46.97	5.93	17.15	18.14	70.91
	PPE						
P_1	1%		53.18	5.36	17.01	17.83	72.49
P_2	2%		53.88	5.42	17.22	18.05	72.52
P_3	3%		52.30	5.08	17.09	17.83	73.42
P_4	4%		50.61	5.67	17.28	18.18	71.83
P_5	5%		49.53	5.72	17.61	18.52	72.00
	Babool						
B_1	1%		49.59	6.88	12.61	14.36	61.34
B_2	2%		52.23	6.12	15.09	16.28	67.87
B_3	3%		47.26	6.85	13.00	14.69	62.11
B_4	4%		47.16	6.80	12.78	14.47	61.99
B_5	5%		48.16	6.70	13.30	14.89	63.20

in its unmordanted form differs considerably to that obtained after mordanting. Color evaluations of ferrous sulphate, alum, and stannous chloride mordanted woolen yarn samples dyed with 20% *A. vasica* extract are shown in Table 3. Application of mordants showed significant variations in colorimetric data, depending upon the extent of interaction developed between woolen yarn, metal, and dye components. All mordanted dyed samples displayed higher color strength values as compared to unmordanted woolen yarn (Fig. 4). This may be attributed to the fact that mordanting process increases interaction between dye and woolen yarn through coordination complex formation, which eventually results in higher dye uptake [8,17,54,55]. Ferrous sulfate mordanted woolen yarn has displayed higher color strength as compared to alum and stannous chloride mordanted samples [56]. The activity sequence of metal salts in terms of color strength values was found to be ferrous sulphate (8.81) > stannous chloride (7.85) > alum (4.10) > control (4.01) dyed samples. This suggests darker shades for ferrous sulphate followed by stannous chloride and alum mordanted samples.

Due to the oxidation of ferrous to ferric form by reacting with atmospheric oxygen and 1:2 metal-dye complex forming ability of iron salts within dyed substrate produced dark shades [51,52]. The ferrous and ferric forms co-exist on the fiber and their spectra overlap, which shifts λ_{max} and results in color change to a darker shade [57]. Moreover, due to higher coordination number of 6, ferrous sulfate forms more stable ternary (1:2 metal-dye) coordination complex within wool fiber resulting in enhanced interaction which eventually increases shade depth of dyed woolen yarn (Fig. 5) [54,55]. On contrary, aluminum and stannous chloride forms weak coordination complexes with the wool fiber and dye molecules. However, alum produced lighter shades and stannous chloride produced brighter shades of varying hue and tone.

From a*-b* values (Table 3) of mordanted samples it is evident that mordanting have shifted color parameters towards red region of color space diagram as compared to unmordanted samples. The lightness (L*) and color saturation values (c*) was found to be least in ferrous sulphate mordanted samples whereas the maximum was found in alum mordanted samples.

3.5.3. Color characteristic evaluation of biomordants

Effect of different bio-mordants on the dyeing property and colorimetric characteristics (CIELa*b* values) of *A. vasica* dyed

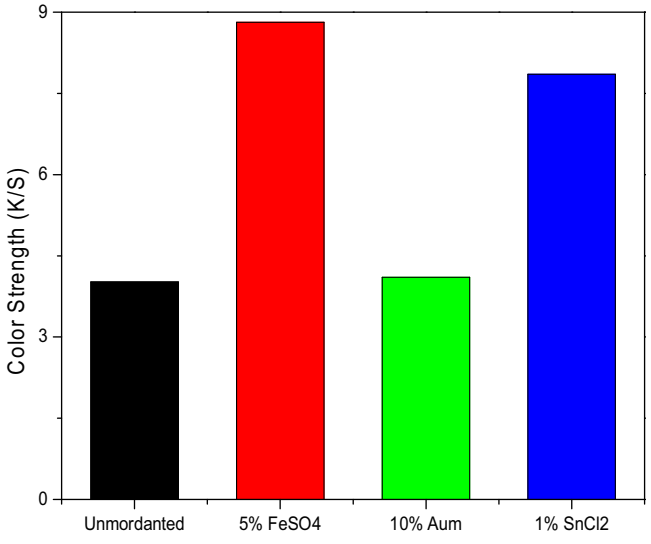

Fig. 4. K/S values of metal mordanted woolen yarn dyed with 20% (o.w.f.) *A. vasica*.

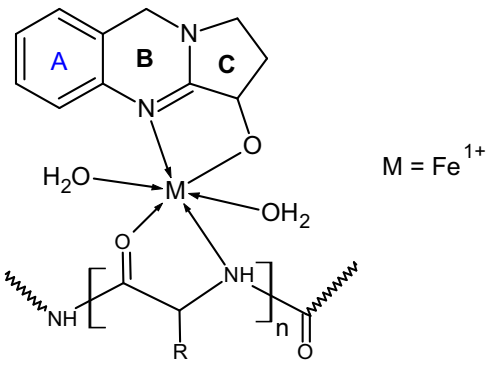

Fig. 5. Wool-Mordant-Dye complex.

woolen yarn are presented in Fig. 6 and Table 3. It can be clearly seen that color strength values of dyed woolen yarn increases with increasing concentrations of biomordants. However, gallnut mordanted samples produced marked and enhanced dyeing effects as compared to PPE and babool mordanted samples. This is attributed to coloring effect and high natural mordant content (Tannins) in gallnut extract showing synergistic effect in conjunction with 20% *A. vasica* dye extract [8,53]. *A. vasica* dyeing with gallnut extract has significantly altered the colorimetric data with low lightness (L*) and chroma (c*) values in comparison to that of control dyeing and have shifted color pellet to yellow region of red-yellow coordinate of color space with hue angle ranging between 70° to 73°. Table 3 shows color measurements for 20% *A. vasica* dyeing with gallnut as biomordant in the concentration range of 1–5%. PPE dyeing produced shades with high lightness (L*) and low chroma (c*) values as compared to that of gallnut mordanted samples (Table 3). Mordanting with PPE caused significant color variations and produced different color gametes depending upon the concentration of the mordant used (Fig. 6). Highest shade depth was shown by 5% PPE concentration although less pronounced than that of corresponding concentration of gallnut.

Unlike gallnut and PPE, babool biomordanting produced light and bright shades of high lightness (L*) and low chroma (c*). High a* and low b* values indicate shifting of color coordinates towards red region of color space diagram. With increasing concentration of babool from 1 to 5%, an increase in color strength (K/S) have been observed as expected from a mordant (Fig. 6) with different color gamuts, hue angle ranging between 61° and 64°. However, babool dyeing shows very low mordanting effect (Low color strength)

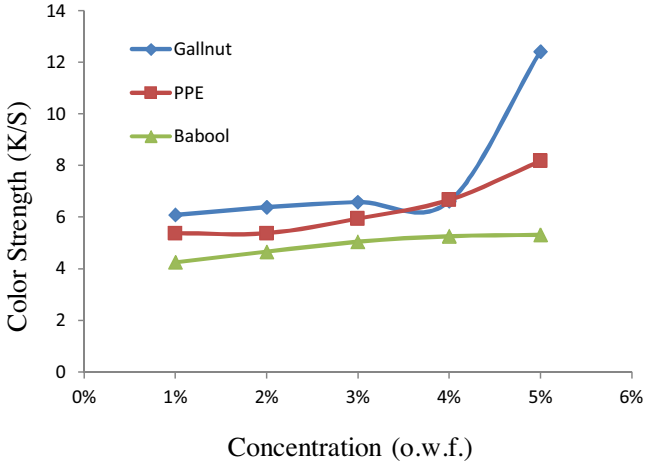

Fig. 6. K/S values of bio-mordanted woolen yarn dyed with 20% (o.w.f.) *A. vasica*.

Table 4
Fastness Properties of control and metal mordanted woolen yarn samples.

S. No.	*A. vasica*	Mordant	Light fastness	Wash fastness			Rub fastness	
				c.c.	c.s.	c.w.	Dry	Wet
C_1	20%		5	4	4–5	4–5	5	4
C_2	15%		5	4	4–5	4–5	5	4–5
C_3	10%	Unmordanted	5	4	4–5	4–5	4–5	4–5
C_4	8%		5	4	4–5	4–5	4–5	4–5
C_5	5%		5	3–4	4–5	4–5	4–5	4–5
C_6	3%		5	3	4–5	4–5	4–5	4–5
	20% (o.w.f.)	**Metal Mordants**						
M_1		Iron	5	4	5	5	5	5
M_2		Alum	5	3–4	5	5	5	4
M_3		Tin	5	4–5	5	5	4–5	4
		Bio-mordanted Gallnut						
G_1		1%	5	3	5	5	4–5	4
G_2		2%	5	3	5	5	4–5	4–5
G_3		3%	5	4	5	5	4–5	4–5
G_4		4%	5	4	5	5	4	4
G_5		5%	5	3	5	5	4	4
		PPE						
P_1		1%	5	4	5	5	4–5	4–5
P_2		2%	5	3	5	5	4–5	4–5
P_3		3%	5	4	5	5	4	4
P_4		4%	5	3–4	5	5	4	4
P_5		5%	5	4	5	5	4	4
		Babool						
B_1		1%	5	4	5	5	4	4
B_2		2%	5	3	5	5	4	4
B_3		3%	5	3	5	5	4–5	4–5
B_4		4%	5	4	5	5	4–5	4–5
B_5		5%	5	3	5	5	4–5	4–5

c.c. = colour change c.s. = colour staining of cotton c.w. = colour staining of wool.
Wt% of mordant and dye raw material is taken with respect to o.w.f. (i.e., 50 g).

probably due to low tannin content as compared to gallnut and pomegranate peel extract.

3.6. Fastness properties

3.6.1. Light fastness

Table 4 presents the light fastness values of woolen yarn samples dyed with *A. vasica* with and without mordant. It is clearly evident that all dyed woolen yarn samples have shown good light fastness rating of 5 on grey scale. Mordanting has no effect on light fastness property of *A. vasica* dyed woolen yarn.

3.6.2. Wash and rub fastness

Wash and rub fastness values of *A. vasica* dyed woolen yarn (Mordanted as well as unmordanted) are given in Table 4. Both metal mordanting as well as biomordanting has remarkably increased color change and staining properties. *A. vasica* control dyeing had a color change of 3–4 and staining of 4–5 on both adjacent cotton and wool fabric. No significant variation has been seen in color change and staining property among the mordanted samples having color change and staining values of 3–4 and 4–5, respectively. Mordanted samples showed better rub fastness property as compared to unmordanted samples. Control dyed samples were found to have good to very good dry and wet rub fastness rating of 4–5. Metal mordanted samples showed very good rub fastness values of 4–5. Gallnut biomordanted samples possess much better rub fastness as compared to PPE and babool mordanted samples (Table 4).

3.7. Comparative colorimetric analysis of biomordant verses metal mordants

This section have been incooporated in order to highlight the comparative analysis of color strength (K/S) and fastness properties of biomordants verses metal mordants and are shown in Table 5. Results from wash fastness and light fastness values show that all the metal mordanted and biomordanted samples were effective in comparison to control dyeing with slight color change variations. Among the biomordanted samples, gallnut in conjunction with *A. vasica* ensured most comparable and enhanced dyeing results with that of metal mordanted samples, hence may be an effective and potential alternative to metal mordants. 3% and 4% gallnut dyeing have comparable color strength values with that of 10% alum and 1% stannous chloride mordanted samples. However, 5% gallnut mordanted samples possesses unexpectedly higher shade depth surpassing the results of metal mordant dyeing with

Table 5
Comparison of fastness properties of biomordants verses metal mordants.

	Control (C_1)	5% Iron	10% Alum	1% Sn	3% Gallnut	4% PPE	4% Babool
Color strength (K/S)	4.01	8.81	4.10	7.85	6.58	6.66	5.04
Color Change	4	4	3–4	4–5	4	3–4	4
Staining	4–5	5	5	5	5	5	5
Dry Rub	5	5	5	4–5	4–5	4	4–5
Wet Rub	4–5	5	4	4–5	4–5	4	4–5

excellent wash fastness results. Among the metal mordants, 5% iron mordanted samples produced darkest shades with lowest lightness (L^*) and least saturation (low chroma value). 5% gallnut and 4% babool mordanted samples show comparable darkening effect as that of 5% iron mordanted samples with almost similar color saturation.

4. Conclusion

An environment friendly approach was presented for development of eco-friendly shades by *A. vasica* as natural dye in conjunction with small amounts of metal salts, natural mordants (biomordant), auxiliary dyeing and washing. The main aim of this study was to investigate dyeing properties on wool in conjunction with small amounts of metallic mordants (ferrous sulphate, alum and stannous chloride) and alternative biomordants (gallnut, pomegranate and babool) and reveal the feasibility of substitution of prevalent metallic mordants by alternative natural mordants as renewable recourses. Results from Table 1, gives an indication that substantial amounts of metal ions remained unexhausted in residual mordant baths which surpass the legal limits of textile effulents from dye industries. Biomordants presented all together different behavior and can serve as an alternative to metal mordants in terms of color characteristics and fastness properties which in turn depends upon their concentrations used with no or minimum environmental impacts and can be discharged into the environment without any chemical treatment. Although, research analysis is required to enhance the biomordanting potential of these biomordants by proper dye standardization procedures to get wide range of ecofriendly shades of acceptable colorimetric and fastness properties.

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