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APPLICATION OF EXTRACTED COLORANT FROM A BI-MIXTURE OF COCOA (*Theobroma cacao* L.) AND CUTCH (*Acacia catechu*) FOR COTTON DYEING

Highlights

- Exploration of cocoa and cutch as a novel binary colourant source for cotton
- MW treatment and bio-mordant have given colorfast shades of high strength
- The selected dyeing variables were a pH 8 binary extract, 80 °C, and 55 min
- ISO standard reveals that eco-mordants have given good to excellent ratings

Abstract

The greener technologies, such as radiation treatment, are gaining worldwide fame due to their promising role in reducing effluent pollution. For the current study, two sources of catechin-based natural colorant in binary form have been appraised for cotton using a statistical approach. Dyeing variables were selected through central composite design under response surface methodology and at dyeing conditions, pre, post, and meta mordanting using eco-friendly anchors. It has been found that 25 mL of the binary extract of pH 9, having 2 g/100 mL of salt at 80 °C for 55 minutes after microwave (MW) treatment up to 4 min, has given an excellent yield (K/S = 2.48). Using 1.5% of tannic acid (TA) before dyeing of cotton has given excellent colour strength up to 4.11 K/S, whereas using myrobalan extraction (2%) after dyeing of cotton with binary extract has given better yield (K/S = 2.85) with good colorfastness. It is concluded that a statistical approach in combination with the MW treatment should be used to explore the coloring behavior of plant dyes for cotton under selected conditions, and the addition of eco-friendly additives (mordants) should be used to get colorfast shades.

Keywords: cocoa leaves, cutch, DPPH assay, green extraction, red sumac, myrobalan.

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INTRODUCTION

The textile industry is one of the major utilizers of various toxic and eco-friendly chemicals [1]. The waste materials in the form of effluents and gases released from textile processing into the environment have increased pollution. These hazardous effluents have widespread effects on global beauty, the community, and living beings. These hazardous effluents, when mixed with fertile land, cause drastic changes in their pH, which in turn, favor soil depletion and infertility, and crop destruction by changing their characteristics. On mixing with aquatic ecosystems, the polluted effluents cause severe changes in their quality parameters [2], which, in turn, cause severe waterborne

diseases and render them unable to be used for domestic and agricultural purposes. Hence, the carcinogenic, toxic, and hazardous effects of textile effluents have forced the global community to rush toward their alternatives. The health-conscious, globe-loving, and eco-friendly community has started campaigning to use natural alternatives, such as natural dyes for all fields [3].

Although there are many sources of natural alternatives for textiles, plant-based natural dyes have wonderful benefits [4]. The most important benefit of plant-based dyes is their potential biological activities, such as anti-viral, anti-cancer, anti-bacterial and fungal, anti-oxidant, etc [5,6]. These dyes are isolated without any particular chemical processing, and after application has no potential carcinogenic effect. However, the carcinogens of their effluents depend upon the use of toxic metals (used as mordants), such as electrolytes of Cu, Cr, Co, Ni, etc. The plant source of natural colorant can grow within the vicinity of other crops and adds value to the growth of crops. Many plant sources are part of the ayurvedic system, where their functional

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moieties have variable functions to cure many seasonal and water-borne diseases [7-9]. In the pandemic era, their effective role was also observed as anti-viral agents to resist against lethal viral infections [10]. Hence, the people, after knowing such wonderful benefits of plant-based dyes, have started the campaign to launch dyed products in the market and forced the traders, researchers, and stakeholders to revive the art of natural dyes for all fields with approved coloring standards. Also, to retain the art of cultural heritage, to save global natural beauty, and to improve community health [11], day by day, the love and eagerness for their use in all fields has been raised. Hence, the revival of green dyes has now become vital for the globe's safety, people's health, and the balance of the ecosystem.

There are many wonderful sources of plant-based dyes that cover the full spectrum of colors. Among these sources, cocoa leaves (*Theobroma cacao* L.) and cutch chips (*Acacia catechu*) have promising benefits [12]. The extract of cocoa leaves powder (Figure 1a) contains catechin (Figure 1c), which has the efficacy to dye cotton, wool, silk, and nylon. Cutch, also known as Katha (Figure 1b), is a well-known source of catechin (Figure 1c) that is used to dye cotton, wool, silk, and nylon. The extract of cutch is also used for many pharmaceutical applications, such as anti-diarrheal, anti-ulcer, antioxidant, anti-diabetic, anti-bacterial, anti-fungal, hemolytic, and anti-inflammatory activities [13]. There are different isolation modes of plant colorants from their crude sources, which include soaking, refluxing, boiling, aqueous extraction, solvent extraction, Soxhlet extraction, etc. However, these methods take a lot of solvent, time, energy, and cost, whereas for prolonged heating, either functional moiety faces hydrolysis or other by-products are also released in high amounts, which, upon application, show their promising effects. Now, conventional approaches have been replaced with modern cost, time, and energy-effective techniques. Among such methods, microwave (MW) treatment is one of the

cheapest and highly effective techniques that has a uniform mode of heating up to the molecular level [14]. These rays transfer energy into solvent molecules in the form of energy packets, which, when they hit the plant boundary, evolve the colorant to a great extent into the medium. By rupturing the cell wall, the mass transfer (colorant) into the solvent occurs, and by this promising binary powder to solvent interaction, the effective yield is observed, which, upon application onto fabric, is noted in terms of color depth (K/S). Another notable benefit of using MW rays is the physical modifications of the cellulosic surfaces without alteration of their chemical nature to enhance their sustainability towards binary colorants. Another issue of fastness can be overcome with the use of metallic salts called chemical mordants [15]. Usually, the salts of Al^{3+} and Fe^{2+}/Fe^{3+} and some organic acids such as tannic acid (TA) are used; however, the salts of Cu^{2+} , Cr^{3+} , Ni^{2+} , Co^{2+} , etc., have come under strict observation owing to environmental regulation [16]. These carcinogenic salts need to be replaced with natural sources called bio-mordants [17]. Plant-based extracts (tannins) have the potential to overcome such eco-issues and to improve colorfastness by developing stable new tints [18].

In our studies, the novelty of the work is the eco-exploration of the binary mixture of plant wastes to isolate the colorant for its application onto cotton. For the first time, using a statistical method, i.e., a central composite design (CCD) under the response surface methodology (RSM), has been utilized to find the significance of cost-effective dyeing variables. Also, for the first time, the addition of MW treatment to stimulate the extract and to activate the cotton fabric surface, as well as the addition of bio-mordants for new shade development, has been done after the utilization of a binary mixture of cocoa and cutch onto fabric. Thus, under the umbrella of sustainable development goals, this study has been made to utilize waste material into useful work, i.e., dyeing of cotton fabric with catechin colorant through mordanting for producing stable colorfast shades.



Figure 1. Cocoa leaves (a), cutch powder (b), and colorant (c).

EXPERIMENTAL

Collection of materials

Dried cocoa leaves (*Theobroma cacao* L.) and Katha or cutch (*Acacia catechu*) woody chips were taken and ground finely. After sieving up to 20 mesh, the powders were kept in airtight jars for further isolation and dyeing uses. Mill-mercerized ready-to-dye cotton fabric (GSM = 70 g/m²) was purchased from the local cloth market of Faisalabad. Bio-mordant sources such as myrobalan (MB, *Terminalia chebula*), and red sumac (SU, *Rhus typhina*)

were also ground finely and sieved up to 20 mesh and stored. Salts of Al^{3+} (alum) and Fe^{2+} (iron sulphate), and TA, neutral soap for washing, formic acid, and sodium carbonate for pH adjustment, purchased from chemical stores, were of commercial grade.

Extraction process

Extraction of dye from binary mixtures (1:1) of plant wastes was carried out by boiling for 60 minutes. The crude mass was separated, and the filtrate obtained, containing catechin, was used for dyeing. For making different sets of

extracts, a binary mixture of cocoa and cutch (2, 4, 6, 8, and 10 g) was mixed with distilled water, keeping the powder-to-water ratio of 1:25. After boiling in an aqueous medium, the crude mass was filtered, and the binary extracts were stored to be used for the dyeing process.

Selection of dyeing variables

For the selection of dyeing parameters and to observe their significance, a central composite design was used under the RSM [19]. The parameters include pH 8–12, salt amount of 1–5 g/100 mL, temperature of 50–90 °C, and time of 25–65 min. were used to make the design (Table S1), where each experiment was run accordingly, and the results were assessed through two-way ANOVA.

Effect of MW treatment

After the selection of dyeing variables, the effect of MW treatment before mixing (RBM) and after mixing of the binary extract (RAM), up to 10 min using a high-power MW irradiator (700 W, 50 Hz). In the comparison, MW heating up to 10 min was also given after dyeing of cotton with the binary extract (RAD). Each experiment was performed separately using a binary extract of pH 9, having 2 g/100 mL of salt for dyeing of cotton at 80 °C for 55 minutes, keeping the dye bath to fabric ratio of 25:1.

Chemical mordanting process

Mordanting in the natural dyes is the prime need, as using the metal salts or organic acid adds value to raise the cotton strength. In this study, two green reported mordants, i.e., Al³⁺ and Fe²⁺ salts, and organic acid (TA) have been used before, after, and during dyeing at selected conditions. First salt solutions were prepared by dissolving 1, 1.5, 2, 2.5, and 3 g of salt in 100 mL of water with occasional stirring. For 1 g of cotton fabric, 25 mL of each mordant solution was employed at 80 °C for 55 minutes before dyeing with binary extracts of cocoa and cutch. The same is the process was done after dyeing cotton with binary extracts under the given conditions. During the dyeing of cotton with binary extract, the solution from salts of metal and organic acid, keeping the mordant to fabric ratio of 25:1, was added slowly till the leveled shade was achieved.

Bio-mordanting process

For comparative studies, the bio-mordants (tannin) from SU and MB have been used. For this purpose, 1, 1.5, 2, 2.5, and 3 g of powder were mixed with 100 mL of water, boiled, and filtered. Extracts of SU and MB were used to coat the fabric before and after dyeing at 80 °C for 55 minutes using a mordant to a fabric ratio of 25:1. The same procedure of mordanting was done onto dyed fabric and during the dyeing of fabric at given conditions.

Spectral analysis of the extract

The binary extracts prepared from cocoa leaves and cutch barks were subjected to UV- visible analysis through a spectrophotometer (STA-4300 Spectrophotometer, China). After irradiation up to 4 minutes, separate as well as binary mixtures were also subjected to analysis within a

range from 380–800 nm using a UV-visual spectrophotometer. The presence of a functional group to the colorant (catechin) from cocoa and cutch has been identified by visualizing particular peaks at specific intensities taken through an ATR-FTIR device (Alginat, USA) in the range of 600–4000 cm⁻¹.

Analysis of the extract and fabric

The fabrics before dyeing were tested for physicochemical changes. For physical analysis fabric before and after MW treatment was scanned under an electron microscope at the Central Resource Lab (CRL), University of Peshawar, Peshawar, Pakistan. For identification of fabric functional groups, cotton fabric before and after MW treatment was scanned in the range of 600–4000 cm⁻¹ using ATR- FTIR (Agilent, USA).

Dyed fabric analysis

Antioxidant activities of the extract and fabrics were performed using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay by following the already documented method of Zhan *et al* [20]. The DPPH free radical scavenging assay was used to assess the antioxidant activity of the extracted dye solution and the dyed fabrics. In absolute methanol, a DPPH solution with a concentration of 0.15 mM was prepared. The optimal absorbance of the working solution was set between 0.8 and 1.0. 96-well plates with a total reaction mixture volume of 100 µL per well were used to set up the reaction. The corresponding wells were then filled with 90 µL of the DPPH solution and 10 µL of each pigment solution. In the control reaction mixtures, 10 µL of methanol was added to 90 µL of the DPPH solution. 96-well plates were incubated for 30 minutes in the dark. A microplate reader was used to measure the absorbance of the reaction mixtures at 517 nm wavelength [20]. The radical-scavenging activity was estimated using the equation below (Eq. 1):

$$\text{Radical Scavenging Activity (RSA)\%} = \left(A_c - \frac{A_s}{A_c} \right) \cdot 100 \quad (1)$$

where A_c is the absorbance of the blank DPPH solution, and A_s is the absorbance of the treated samples.

The dyed fabrics obtained from isolation, dyeing, and mordanting were tested in the CIE Lab system using Data Colour SF 600 (USA), and tonal expressions (L^* , a^* , b^* , C^* , and h) were also determined. For observing shade stability, ISO standard methods for light, washing, and rubbing were used. For washing fastness through ISO 105 C03, neutral soap was used, and after their washing, the results were rated on the grey scale. Similarly, for light fastness through ISO 105 B02 using a Xenon lamp, dyed mordanted fabrics were tested, and the results were at blue scale. For rubbing fastness through ISO 105 X12, the fabrics were crocked using 10 turns both in dry and wet conditions, and the results were analyzed with a grey scale.

RESULT AND DISCUSSION

Selection of coloring conditions

Dyeing of fabric at selected conditions always gives a firm shade because the equilibrium of the dye bath can be

achieved at selected conditions to get the desired results. In this study central composite design has been employed, and the results have been assessed statistically through two-way ANOVA analysis. The dyeing results after performing 31 experiments, 7 given in Table 1, reveal that the extract of pH 9 obtained from 8 g of the binary powder

(4:4 catch:cocoa ratio) having 2 g/100 mL of salt, when employed onto cotton at 80 °C for 55 min, has given an excellent yield. The model used for the analysis of dyeing variables (Table 1) and their significance in the coloration of cotton with binary mixtures has been found fit ($p = 0.00$) and linear ($p = 0.00$).

Table 1. Assessment for the significance of dyeing variables through two-way analysis of variation.

Source	DF	Adj SS	Adj MS	F-Value	p-Value
Model	17	0.462	0.027	92.79	0.000
Linear	5	0.185	0.037	126.24	0.000
Powder	1	0.148	0.148	504.85	0.000
Time	1	0.018	0.018	64.02	0.000
Temperature	1	0.008	0.008	29.55	0.000
Salt	1	0.006	0.006	22.13	0.001
pH	1	0.003	0.003	10.66	0.009
Square	5	0.178	0.035	121.88	0.000
Powder*Powder	1	0.095	0.095	325.93	0.000
Time*Time	1	0.059	0.059	202.40	0.000
Temperature*Temperature	1	0.076	0.076	260.24	0.000
Salt*Salt	1	0.061	0.061	210.01	0.000
pH*pH	1	0.002	0.002	9.56	0.011
2-Way Interaction	7	0.098	0.014	47.75	0.000
Powder*Time	1	0.003	0.003	11.61	0.007
Powder*Temperature	1	0.018	0.018	63.59	0.000
Powder*Salt	1	0.004	0.004	14.91	0.004
Powder*pH	1	0.066	0.066	226.22	0.000
Time*Temperature	1	0.000	0.000	3.19	0.104
Time*Salt	1	0.003	0.003	13.30	0.004
Temperature*pH	1	0.000	0.000	2.17	0.172
Error	10	0.002	0.000	-	-
Lack-of-Fit	6	0.002	0.000	3.30	0.134
Pure Error	4	0.000	0.000	-	-
Total	27	0.465	-	-	-
Model Summary	<i>S</i>	<i>R</i> ²	<i>R</i> ² (adj)	<i>R</i> ² (pred)	
	0.0171	99.4%	98.3%	-	

The role of coloring time has been found highly significant because dyeing for 55 min has given excellent yield. During the short time dyeing, the dye molecules move slowly to sorb, whereas dyeing for a long time, the continuous heat favors desorption as well as dye hydrolysis, due to which, on analysis, low color yield is found [21]. However, for 55 min, equilibrium of the dye bath may be achieved, which results in high color yield onto cotton. Statistically, the role of dyeing time ($p = 0.00$) has been found highly significant individually, whereas in the combination, i.e., two-way interaction with time (55 min.) and salt (2 g/100 mL) has also been found significant ($p = 0.00$).

Along with contact time, the heating level also plays a role in the bio-coloration of cotton. At low heat levels, the interaction of fabric with binary colorant becomes less due to the low kinetic energy of the dyeing system. The dyeing above the selected level (>80 °C) may give desorption or hydrolysis of dye into by-products, which, when sorbed onto fabric, show less color depth. At 80 °C, the rate of dyeing lies in equilibrium with the rate of desorption, and maximum dye molecules are sorbed onto cotton to give high strength up to the maximum extent. Statistical analysis shows that the role of temperature in the presence of salt (2 g/100 mL), dye bath pH (pH 9), and time (55 min) has shown highly significant results ($p = 0.00$). Thus, cotton

dyeing with a binary mixture at 80 °C for 55 min should be done. For cotton dyeing, the role of the dye bath's nature (pH) can also be seen as promising. The nature of the colorant, the type of fiber, and the dyeing methods add value to the good and leveled coloration with maximum strength. Usually, cellulosic dyeing is favored by an alkaline medium, which reveals that dye molecules interact with the terminal -OH of cotton through H-bonding to give a stable shade [22]. However, on the further rise of pH, the dye and fiber may become more ionic, which repel each other and form a shade of low tint strength (*K/S*). The addition of table salt in cotton dyeing has a potential role because its presence is used to create an atmosphere in the dye bath for the interaction of the cotton cellulosic -OH site with the -OH site of the dye in the range of attractive forces. The low salt amount cannot give this situation, where the too high amount causes the aggregation of colorant onto fabric and in the dye bath causes dye molecules to remain unfixed. On washing, a lot of dye molecules are washed away, and a light shade of less strength is found. Using 2 g/100 mL of table salt in the dye bath tries to neutralize the negative charge on cotton and to reduce maximum repulsion between dye anion and cellulosic anions [23]. Thus, the selected amount of salt (2 g/100 mL) gives maximum exhaustion of dye towards fabric to produce dark shades of

high strength. Statistically, through two-way ANOVA analysis, it can be seen that the role of salt (2 g/100 mL) in the presence of temperature (80 °C) and time (55 minutes) using a dye bath of pH 9 as dyeing variables is highly significant ($p = 0.00$). Hence, the role of selected dyeing variables has been found significant in the coloration of cotton with binary mixtures of cocoa and cutch. Hence, on assessment, it has been found that a dye bath of pH 9, having 2 g/100 mL of salt, if used to dye cotton at 80 °C for 55 min, the acceptable results can be obtained.

Promising role of microwave rays

Now, using these selected variables, the role of MW treatment before mixing, followed by dyeing RBM, after mixing before dyeing RAM, and after dyeing RAD has been studied. MW treatment to both extract and the cotton fabric adds value promisingly in raising the value of color depth [24]. Previously, our studies reported that MW treatment heats the materials inside by transferring energy outside, which, in turn, gives the desired results. In an isolation system, these rays provide energy to polar solvent molecules, which, when they collide with the cell wall, break the boundary and evolve the colorant to the maximum extent [25]. Secondly, the big clusters of colorant molecules, if isolated, are hit by these rays where solvent molecules full of energy break them into small sizes that find a more significant chance to interact with fabric through ionic bonds [26]. Hence, these rays cause selective and uniform action to yield high mass (colorant) by giving fast solid-liquid interaction [27]. The same is the situation found in our studies (Figure S1), where these rays, when they hit the plant extract separately for 4 minutes, where the cluster of colorant broke down, and upon mixing, followed by dyeing, showed a high yield ($K/S = 2.48$). Hence, using selective dyeing conditions, the irradiation of extracts from cocoa and cutch and fabric separately for 4 min, and on mixing, followed by their application, has shown promising results ($K/S = 2.48$).

The other factor is the MW treatment on cotton, which has also been found to be significant. The physical modification of the fabric surface, which has been verified by scanned images displayed in Figure S2 (A-B). The peeled surface has enhanced the sorption attitude of cotton physically in such a way that the binary extract (separately MW treatment up to 4 min), when used to dye, has shown a high yield. The previous studies show that no change in the functional nature of the cellulosic unit of cotton has been observed after the MW treatment. Thus, the MW treatment has shown two-fold benefits, i.e., physical modification of fabric without any chemical change and mass transfer kinetics in aqueous medium to give high color yield of colorant onto cotton.

Physicochemical analysis of extracts and fabric

The antioxidant activity of the extracts, dyed and mordanted, and dyed fabric (Table S2) reveals that after radiation, the radical scavenging activity by catechin from the binary mixture has been improved, which, before any treatment, the fabric showed the activity up to 29%, whereas after radiation the tuning of surface by the MW

treatment has improved its action against oxidation. Similarly, application of catechin onto fabric for dyeing has improved the behavior up to 46%. On mordanting with Fe^{2+} as a chemical and MB as a bio-mordant, the antioxidant action of the fabric has been greatly increased. Also, when the extract was checked before and after radiation, the activity was enhanced almost double or four times, which showed that MW treatment of the extract, fabric, and addition of mordant has improved the antioxidant behavior beneficial for the warrior. The same work has been done by Zhan *et al.* [20], which also reveals that both the extract and dyed fabric have shown good antioxidant activity. This good antioxidant activity is due to the presence of multiple -OH groups and conjugation of colorant from the binary mixture of cocoa and cutch. These OH groups donate an electron or an H atom to neutralize the free radical of DPPH, whereas conjugation by multiple benzene rings present in the binary colorant (catechin) also adds value in radical stabilization to improve its antioxidant behavior. In the presence of metal salt (Fe^{2+}), it forms chelates with the phenolic side of catechin and the -OH side of the cellulosic unit from cotton, due to which the scavenging activity and antioxidant behavior are raised. Thus, mordanting has improved the antioxidant activity of the isolated binary colorant (catechin) when used to dye the fabrics after mordanting. The structural groups responsible for bonding with cotton by cocoa and cutch colorant have been studied through spectra under the ATR/FTIR technique. The broad peak obtained at 3415 cm^{-1} and 2944 cm^{-1} , and the C-O-C at 1061 cm^{-1} showed the existence of -OH, -CH₂, and R-O-R groups (Figure S3 a-b). After the MW treatment, these spectral intensities given by functional groups have not altered their positions. Previous studies also show that this treatment does not cause any change in the chemical nature of the cellulosic unit of cotton. Similarly binary extract was scanned for observing optical density and found that the maximum spectra were found at 473 nm before and at 475 nm after radiation (Figure S4).

Inorganic mordanting for stable shades

Mordanting in the natural dyeing of cotton gives an affinity towards fabric as well as a new colorfast look [29]. Although many plants yield brilliant and pleasant shades, owing to their stability towards the light, soaping, crocking, perspiration, dry cleaning, etc., always remains the question. To overcome the issue of poor shade fastness and less stability, metal salts, usually the transition metals, are used [30,31]. In this study, salts of Al^{3+} and Fe^{2+} and organic acids, such as TA, have been employed before (pre), after (post), and during (meta) dyeing of cotton with binary extracts of cocoa and cutch at optimum conditions. The results given in Figure 2 (a-c) showed that 1.5% of TA before dyeing, 1.5% of TA after dyeing, and 1.5% of TA during dyeing produced shades of high color strength with tonal expressions (Table 2). But overall, in comparison to using a binary extract of cocoa and cutch, mordanting before dyeing of cotton with 1.5% TA (pretreatment) has produced shades of excellent strength ($K/S = 4.11$). The shade developed after dyeing the application of the

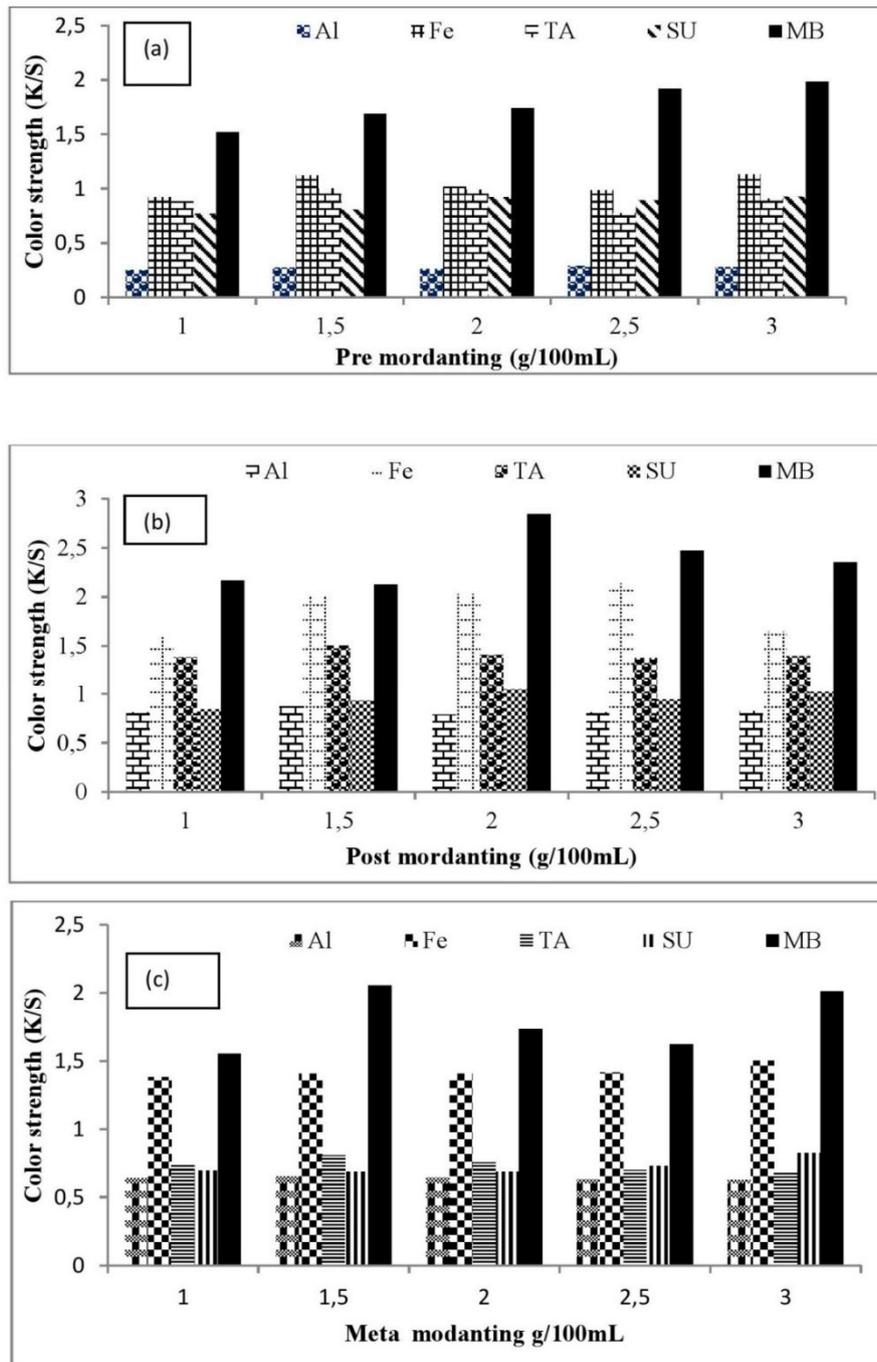


Figure 2. Color strength of dyed cotton before (a), after (b), and during (c) chemical and bio-mordanting.

Table 2. Tonal Values of optimum dyed fabric before, after, and during chemical and bio-mordanting

Mordant used	Colour strength (K/S)	L^*	a^*	b^*	C^*	h
TA (1.5% before dyeing)	4.11	56.05	11.08	17.74	20.92	58.02
Fe ²⁺ (2.5% before dyeing)	2.13	61.96	20.82	20.07	28.92	43.95
Al ³⁺ (1.5% before dyeing)	0.87	73.23	23.19	16.97	28.73	36.21
SU (2% after dyeing)	1.05	71.53	23.06	17.56	28.98	37.29
MB (2% after dyeing)	2.85	71.76	12.76	27.22	30.06	64.89

TA – tannic acid, Fe²⁺ – FeSO₄, Al³⁺ – Alum, SU – red sumac, and MB – myrobalan.

optimum amount of TA (1.5% before dyeing) is reddish yellow in tone ($\bar{a}^* = 11.08$, $\bar{b}^* = 17.74$) with good chromacity and hue value ($C^* = 20.92$, $h = 58.02$), with a dark appearance tone ($L^* = 56.05$). Thus, if TA is selected as an eco-mordant, then its pre-treatment onto dyed cotton has been recommended. This is because TA possesses -OH as the bonding site, which interacts with -OH of cotton and -OH from binary sites of cocoa and cutch phenolic (catechin) through H-bonding. Thus, the MW treatment of cotton and binary extract has also reduced the amount of TA used and recommended its post treatment to get a leveled shade.

Using salts of Al^{3+} (1.5% before dyeing), followed by dyeing of cotton with binary extracts at optimum conditions, has given excellent strength ($K/S = 0.87$). Similarly, after dyeing cotton with binary extracts, the application of 1.5% of the Al^{3+} salt (post-treatment) has given a better yield up to 0.65; however, during the dyeing of cotton (meta-treatment), the addition of 2.5% of the Al^{3+} salt has given a very low yield up to 0.29. Overall, the pretreatment of cotton with 1.5% of the Al^{3+} salt after dyeing has furnished a shade of high strength on dyeing with the binary extract of cocoa and cutch (Figure 2 a-c). The shade developed after pretreatment with Al^{3+} - salt treatment is much brighter ($L^* = 73.23$), with reddish yellow tone ($\bar{a}^* = 23.19$, $\bar{b}^* = 16.97$) having high saturation and hue value ($C^* = 28.73$, $h = 36.21$). This is because Al^{3+} forms the stable dye complex through coordinated covalent bonds. However, Al^{3+} only makes the shade bright due to a lack of d-orbital, but it has the potential to give firm shade. Hence, for binary mixtures of cocoa and cutch, the pre-treatment of cotton with Al^{3+} salt before dyeing has been recommended to get colorfast, bright shades.

Iron salt (Fe^{2+}) is one of the eco-friendly mordants that have the potential to change the shade, strength, and fastness if used before, after, and during dyeing of cotton (Figure 2 a-c). In our studies, pre-iron mordanted cotton (2.5%) on dyeing with binary cocoa and cutch extract has given an excellent yield K/S value up to 2.13, whereas after dyeing of cotton, the usage of 3% of Fe^{2+} salt has given a better yield K/S value up to 1.51. However, during the dyeing of cotton with binary extract, the inclusion of 3% of Fe^{2+} salt solution has given a good yield K/S value up to 1.14. Overall, the usage of Iron salt before dyeing of cotton (pre-treatment) up to 2.5% has the potential to develop a darker shade with a dark reddish yellow tone ($L^* = 61.96$, $\bar{a}^* = 20.82$, $\bar{b}^* = 20.07$) of high saturation and hue level ($C^* = 28.92$, $h = 43.95$). The Fe^{2+} salt has low reduction power, and it interacts with -OH of cotton and -OH from binary extract through a coordinated covalent bond to give dark shades [32]. Comparatively, among chemical mordants used, the pre-treatment of cotton has favored producing a high colour yield with good fastness properties. The proposed interaction of the chemical mordant with dye and cotton has been displayed in Figure S6 (a).

Organic mordanting for stable shades (Bio- mordant)

Bio-mordants are bio-active molecules from natural sources that have the potential to replace toxic chemical mordants. For cotton dyeing, many bio-mordants have

been explored, where tannin-based bio-mordants have been recommended to get colorfast shades. Usually, oak galls, pomegranate, and myrobalan as tannin sources have been used in the dyeing of fabrics with plant extracts [33]. These bio-actives have many ayurvedic abilities as well as biological activities that are transferred onto cotton before, after, and during dyeing with plant colorants. These bio-mordants have mostly -OH as binding sites that interact with -OH of cellulose and -OH of colorant via extra H-bonding to develop colorfast shades. Also, the addition of a conjugated system from bio-mordant adds value to enhance its properties [34]. Thus, bio-mordants are now gaining fame due to their clean and green, promising nature as an alternative to their toxic counterpart. In this study, the two sources of tannin bio-mordant, i.e., MB and SU, have been used before, after, and during dyeing of cotton with binary extracts at selected conditions (Fig. 2 a-c). SU is often used as a mordant source both in the dyeing of fabrics and a coating (bio-mordanting) of fabrics called bio-mordanting [35].

Before dyeing, the coating of irradiated cotton with 3 g/100 mL of SU, after dyeing with 2 g/100 mL of SU, and during dyeing with 3 g/100 mL of the SU extract, has given high tint strength. Based on excellent color strength, our study recommends that after dyeing of irradiated cotton with binary extracts of cocoa and cutch, the post treatment of dyed fabric with 2 g/100 ml of SU should be done to get a high yield (K/S 1.05). The shade appearance revealed that red sumac (SU), as a post-bio-mordant, has produced a bright reddish-yellow tone ($L^* = 71.53$, $\bar{a}^* = 23.06$, $\bar{b}^* = 17.56$) with the saturated hue of good chromacity ($C^* = 28.98$, $h = 37.29$). MB is another well-known source of tannin-based bio-mordant, which has the potential to give a saturated, stable hue of high strength onto fabric. The study revealed that before dyeing the coating of cotton with 3 g/100 mL of MB extract, after dyeing with 2 g/100 mL of myrobalan extract, and during dyeing, the addition of 1.5 g/100 mL of myrobalan extract has given a high yield. Comparatively, based on high strength, the utilization of 2 g/100 mL of MB extract after dyeing of irradiated cotton with binary extract (post-treatment) has given the highest yield ($K/S = 2.85$). The shade produced by post-bio-treatment with myrobalan extract is bright reddish yellow in tone ($L^* = 71.76$, $\bar{a}^* = 12.76$, $\bar{b}^* = 27.22$), having good saturation and high hue value ($C^* = 30.06$, $h = 64.89$). The proposed interaction of dye with cotton and mordant has been given in Figure S6 (b). Hence, overall post-treatment of cotton with eco-friendly bio-mordant, i.e., MB, has been recommended to develop colorfast shades of excellent color strength if the fabric is dyed under the given conditions.

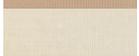
Colorfastness of dyed fabrics

Colorfastness is one of the main tools for the assessment of shade quality and stability [36]. To have good and acceptable fastness results, many factors such as fabric type, mode of isolation, mordant type, dyeing methods and conditions, and dye distribution play their role. Thus, to improve this dyeing aspect, a careful process of

dyeing and treatment with auxiliaries, such as fixers or mordants, is needed [37]. The even distribution of dye molecules into the voids of fabric after MW treatment and the use of eco-friendly mordant to give firm shade play their role [38]. In our study, the selected amounts of eco-friendly anchors that were used before, during, and after dyeing of cotton have formed a stable metal dye complex to give colorfast shades (Table 3). The formation of a stable metal

dye complex onto cotton using metal salts, stable extra H-bonding due to phenolics of bio-mordant (tannin), and an additional conjugation system have jointly played their role in resisting the shade from fading. The good light fastness is due to the excitation of electrons from the metal, the sorption of dye complex onto cotton, and the oxidation power of the metal.

Table 3. Shade fastness rating of mordanted cotton fabric dyed with cocoa and cutch binary extracts

Mordant used	Light fastness	Wash fastness		Dry rubbing Fastness	Wet rubbing fastness	Shades
		Colour stain	Colour change			
Without mordant	4	4	¾	4	¾	
TA 1.5% before dyeing	5	4/5	4/5	5	5	
TA 1.5% after dyeing	6	4/5	4/5	5	4/5	
TA 1.5% meta	5	4/5	4/5	5	4/5	
Fe ²⁺ 2.5% before dyeing	6	4/5	4/5	5	5	
Fe ²⁺ 3% after dyeing	5	4/5	4/5	5	4/5	
Fe ²⁺ 3% meta	5	4/5	4/5	5	4/5	
Al ³⁺ 1.5% before dyeing	6	4/5	4/5	5	5	
Al ³⁺ 1.5% after dyeing	6	4/5	4/5	5	5	
Al ³⁺ 2.5% meta	5	4/5	4/5	5	4/5	
SU 3% before dyeing	6	4/5	4/5	5	5	
SU 2% after dyeing	5	4/5	4/5	5	4/5	
SU 3% meta	5	4/5	4/5	5	4/5	
MB 3% before dyeing	6	4/5	4/5	5	5	
MB 2% after dyeing	5	4/5	4/5	5	4/5	
MB 1.5% meta	5	4/5	4/5	5	4/5	

TA – tannic acid, Fe²⁺ – FeSO₄, Al³⁺ – Alum, SU – red sumac, and MB – myrobalan.

Wash fastness also depends upon mordanting, where dye and -OH of the cellulosic unit of cotton impart their promising role to yield a stable shade before and after mordanting. Similarly, polyphenolics from bio-sources form -OH of cotton and -OH of tannin, which adds value in prohibiting soap action to remove the color intensity (Table 3). Similarly, sorption of colorant on surface-modified cotton treated with eco-mordants (chemical or bio) also resists crocking up to 10 turns to detach the colorant. Hence, overall, our studies reveal that if cotton is MW treated up to 4 minutes and used for dyeing with a binary mixture of extract after mordanting, the colorfast rating is observed (Table 2).

CONCLUSION

The need for greener products is the demand of healthy environment, particularly for textiles and allied

fields. The appraisal of waste agri-material, such as cocoa leaves and cutch chips for cotton, has been done through statistical analysis followed by mordanting. The inclusion of MW treatment for effective colorant yield and green chemicals for getting colorfast shades has made the process more sustainable with less effluent load. The importance of the statistical method, i.e., central composite design, to observe the significance of selected dyeing variables has made the dyeing of cotton with plant extracts cost, time, and energy saving. Using this treatment, new agri-waste dye-yielding plants can be mixed and utilized for dyeing of natural and synthetic fabrics. Also, new mordants for shade development can be found and employed for greener dyeing of synthetic and natural fabrics with biological activities. Our studies recommend that, using selected dyeing conditions, the binary mixtures of other plant wastes can be considered as a source for future

recommendations of natural dyes for natural and synthetic fabrics.

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University Faisalabad , Pakistan**PRIMENA EKSTRAHOVANE BOJE IZ MEŠAVINE KAKAOA (*Theobroma cacao* L.) I BAGREMA (*Acacia catechu*) ZA BOJENJE PAMUKA**

Ekološki prihvatljivije tehnologije, kao što je tretman zračenjem, stiču svetsku slavu zbog svoje obećavajuće uloge u smanjenju zagađenja otpadnih voda. U ovom radu, efekti dva izvora prirodne boje na bazi katehina u smeši na pamuk su procenjena korišćenjem statističkog pristupa. Promenljive bojenja su odabrane putem centralnog kompozicionog dizajna i metodologije površine odziva i pod uslovima bojenja, pre, posle i meta-mordantovanja korišćenjem ekološki prihvatljivih ančora. Utvrđeno je da je 25 mL binarnog ekstrakta (pH 9), koji sadrži 2 g/100 ml soli na 80 °C tokom 55 minuta nakon tretmana mikrotalasnom zračenjem do 4 min, dalo odličan prinos (K/S = 2,48). Korišćenje 1,5% taninske kiseline (TA) pre bojenja pamuka dalo je odličnu jačinu boje do K/S = 4,11, dok je korišćenje ekstrakcije mirobalanom (2%) nakon bojenja pamuka binarnim ekstraktom dalo bolji prinos (K/S = 2,85) sa dobrom postojanošću boje. Zaključeno je da bi statistički pristup u kombinaciji sa mikrotalasnom obradom trebalo koristiti za ispitivanje ponašanja biljnih boja za pamuk pod odabranim uslovima, a dodavanje ekološki prihvatljivih aditiva (mordanta) trebalo bi koristiti za dobijanje postojanih nijansi boje.

Ključne reči: lišće kokoe, bagrem, DPPH analiza, zelena ekstrakcija, crveni ruj, mirobalan.

NAUČNI RAD