Promising Effect of Metallic Mordants on Colorimetric Physiognomy of Dyed Cotton Fabric Employing Banana (Musa Sapientum) Agricultural Waste

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Abstract This analysis intends to unveil the effect of metallic mordants on colorimetric properties of ecologically dyed cotton fabric using banana floral stem sap (BFS). Natural dye retrieved from banana floral stem by roller squeezer machine. Pre-mortanting action was performed by potassium alum, iron (II) sulphate, copper (II) sulphate and tin (II) chloride. Pre-mortanted specimens were dyed at 100°C for 60 minutes. Dye fiber binding actions was determined by FTIR-ATR spectra. Effect of metallic mordants were calculated using CIE L*a*b* color space in terms of colorimetric properties viz. color coordinates value i.e. lightness (L*), redness (a*), yellowness (b*), color saturation (C*) and hue angle (h°); color strength (K/S) value; degree of color levelness and brightness index (BI). Though iron (II) sulphate treated samples exhibited height color saturation but uneven physiognomy was observed. Among them best colorimetric appearance yielded in case of alum. This reports forecast a sustainable pathway for effective utilization of agricultural waste i.e. banana floral stem sap for coloration of cotton fabric.

Keywords Eco-friendly Dyeing, Banana Floral Stem Sap, Natural Dyestuff, Metallic Mordants, Colorimetric Properties, Color Levelness

1. Introduction

The application of natural dyes for textile dyeing purposes declined to a great extent after the innovation of synthetic dyes in 1856 [1]. Synthetic dyes are widely available and have moderate to excellent color fastness properties and produce a wide diversity of colors. But discharged effluents from textile industries are severely endangering the human health and aquatic environment [2].

In this regards, the use of non-allergic, non-carcinogenic, non-toxic, very brilliant, rare color idea and eco-friendly natural dyes on textiles is a re-emerged soaring interest around the globe. It is a potential viable ‘Green chemistry’ for avoiding the uses of hazardous synthetic dyes for their various growing environmental and health concerns [3-5].

Natural dyes are safe and biodegradable in nature which can be obtained from different sources such as plants, insects/animals, microbes and minerals, renewable and sustainable bio resource products [4]. Moreover, they have many excellent functional properties such as mosquito repellency [6], antimicrobial and antiviral properties [3], flame retardency [7], UV protection properties [8], aroma properties [9], wound healing and anti-inflammatory properties [10], moisturizing and refreshing effects [11].

But tragically natural dyes show low exhaustion, poor to moderate wash and light fastness properties [12, 13]. Standardized method for dye extraction, color yield, complexity of dyeing process, limited shade, reproducible results; blending problems are also key constraints [14]. Most attempts for overcoming these problems involved the use of metallic salts as mordants. Commonly used mordants are aluminium potassium sulfate, stannous chloride, ferrous sulfate and copper sulfate. The metal ions can act as electron donor to form coordination bonds with the dye molecules.

Among numerous natural dye, banana floral stem sap is promising sustainable agricultural bio waste dye source. Banana plant parts viz. leaves engaged with cotton coloration [5]; pseudostem sap for mordant [15] and functional finishing [7] and pseudo stem fiber used for dye adsorbent [16]; banana peel for antibacterial activity and UV protection property of cotton fabrics [8] successfully. Dyeing time and temperature had optimized in our previous studies for cotton coloration using BFS, where lower depth of shade and limited color variety was observed [17, 18]. And till now no investigation had carried out to improve the dye fiber bond for boosting depth of shade and color variety of cotton coloration by BFS using metallic salts.

This present study attempts to extend the depth of shade
and produce variety of color on coloration of cotton fabric using banana floral stem sap as natural dye together with various metallic mordants. Effective exploitation of bio-resource waste of banana plant was also aim of this work.

2. Experimental

2.1. Materials and Methods

2.1.1. Materials

Commercially scoured-bleached of 100% cotton knitted single jersey structure fabric having areal density of 175 grams per square meter was collected from “HI-FASHION COMPOSITE TEXTILES LTD”, Joydebpur, Gazipur, Bangladesh for this experiment. Table 1 depicts the color co-ordinates of the fabric used for this research work.

<table>
<thead>
<tr>
<th>WI</th>
<th>BI</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>c*</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>68.38</td>
<td>94.19</td>
<td>93.68</td>
<td>-0.30</td>
<td>3.67</td>
<td>3.68</td>
<td>94.74</td>
</tr>
</tbody>
</table>

2.1.2. Dyes & Chemicals

Banana floral Stem (Musa sapientum) was collected from Santosh area, Tangail-1902, Bangladesh. Potassium Alum \([\text{Al}_2\text{K}_2(\text{SO}_4)_4]\), Iron (II) sulfate heptahydrate (FeSO\(_4\).7H\(_2\)O), Copper (II) sulfate pentahydrate (CuSO\(_4\).5H\(_2\)O) and Stannous chloride pentahydrate (SnCl\(_2\).5H\(_2\)O) procured from merck, Germany. The ISO Standard soaping agent without optical brighter, James heal, England were used for removing unfixed dye. All chemicals were laboratory grade and employed without any purification.

2.2. Methods

2.2.1. Sampling Plan

Different samples are identified as below

<table>
<thead>
<tr>
<th>Sample types</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated / Control/ reference sample</td>
<td>A</td>
</tr>
<tr>
<td>Potassium Alum treated sample</td>
<td>B</td>
</tr>
<tr>
<td>Iron (II) sulfate treated sample</td>
<td>C</td>
</tr>
<tr>
<td>Copper (II) sulfate treated sample</td>
<td>D</td>
</tr>
<tr>
<td>Stannous chloride treated sample</td>
<td>E</td>
</tr>
</tbody>
</table>

2.2.2. Natural Dye Extraction

Dye used in this study was extracted according to our pervious investigations [17, 18]. Briefly, Banana (Musa sapientum) floral stems were detached from banana tree and washed. Fresh floral stem of the banana was cut into one meter pieces using cutlass and then pieces were sliced. Sap was extracted from floral stem by roller squeezer machine. Sap was filtrated by a nylon strainer and stored in plastic container. The sap was kept in a cool place and was prevented from sun rays to avoid evaporation and possible reaction for photo-catalytic degradation.

2.2.3. Mordanting

Cotton fabric samples were subjected to pre-mordanting with metallic mordants by 5 g/L at 100°C for 60 minutes. After soaking overnight, the mordanted samples were squeezed and air dried in flat dryer machine (MESDAN, Italy). The material to liquor ration had kept 1:20 in pre-mordanting action [17, 18].

2.2.4. Dyeing

The dyeing action was ended according to our previous study [17, 18]. Briefly, dyeing had carried out according to exhaust method by Infra-red lab sample dyeing machine (XIAMEN RAPID, China) at 100°C for 60 minutes. Then the dye bath was cooled at 40°C. Samples were washed at room temperature and air dried in flat dryer machine (MESDAN, Italy). Then soaping was performed for removing unfixed dye from the fabric surface by 0.5 g/L ISO standard soap at 80 °C for 10 minutes. For both dyeing and soaping, the material to liquor ration had kept 1:20.

2.2.5. FTIR-ATR Spectra

FTIR-ATR spectra of scoured bleached cotton and dyed specimens were determined using FTIR spectrophotometer (PerkinElmer Spectrum Two, UK). Specimens were directly
fitted on the respective place of Universal ATR of the machine for dye-fiber bonding characteristics evaluation.

Figure 4. Binding among tannic acid, flavonoids (Luteolin) of banana floral stem sap with cotton surface [19, 27].

2.2.6. Determination of Color Coordinates Value

The color coordinates of the dyed samples were determined based on the CIE Lab system via dual beam reflectance Data-color Spectroflash (SF 650X, USA) keeping the setting: Illuminant D65, Medium area view, Specular included and CIE 1964 supple-mental standard observer (10° observer). Each sample was folded twice to give an opaque view with four plies and the color coordinates value was measured automatically [17, 18].

2.2.7. Determination of Degree of Color Levelness

The degree of levelness was measured according to Uddin, Mohammad Gias (2015) [20]. Briefly, color difference, $\Delta E$ value was measured by equation 1.

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

Where, $\Delta L^*$ = $L^*$ sample $-$ $L^*$ standard, $\Delta a^*$ = $a^*$ sample $-$ $a^*$ standard and $\Delta b^*$ = $b^*$ sample $-$ $b^*$ standard

2.2.8. Determination of Color Strength

The color strength (K/S value) of the dyed samples was measured by datacolor spectrophotometer based on KubelkaMunk theory (Equation 2) [21].

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

Where, R=Reflectance of an incident light from the dyed material, K=Absorption and S= Scattering coefficient of the dyed fabric. The K/S values were determined at the maximum absorption wavelength ($\lambda_{max}$=360) at which reflectance value is lowest.

2.2.9. Determination of Brightness Index

Brightness index was measured as per the standard (ISO-2470-1977) [20] method using equation 3.

$$\text{Brightness index} = \frac{\text{Reflectance value of the substrate at } 360 \text{ nm}}{\text{Reflectance value of white diffuser or white tile at } 360 \text{ nm}}$$

3. Results and Discussion

3.1. FTIR-ATR Characterization

Figure 5 represents the IR spectra of scoured bleached (1) and dyed specimen employing BFS (2). The peaks value of spectra assigned as:

- A broad band at 3335.4 cm$^{-1}$ attributed to $-\text{OH}$ stretching vibration for H bonded H$_2$O uptake [23].
- Two peaks at 2915.2 cm$^{-1}$ and 2858.6 cm$^{-1}$ corresponds asymmetric and symmetric stretching of long methylene (-$\text{CH}_2$-) chain for residual wax on cotton [24].
- For adsorbed H$_2$O into the fabric specimen, peaks appeared at 1638 cm$^{-1}$ [25]
- Peak observed at 1423 cm$^{-1}$ which attributed for C-H wagging of carbohydrate and lignin [24,25]
- For presence of the band at 1323 cm$^{-1}$ endorsed for lignin [26].
- Both peaks at 1153cm$^{-1}$ and 1109cm$^{-1}$ corresponds for asymmetric ether linkage (-C-O-C-) [24].
- For cellulose, hemicellulose and minor lignin contribution Spectra (1) & (2) exhibited strong band at 1028.3 cm$^{-1}$ due to C-O-C symmetric stretching di-alkyl ether linkages and C-O stretching vibration [26].
- Peak at 898 cm$^{-1}$ attributes for $\beta$ glycoadic likage and asymmetric out of phase ring stretch of C$_3$-O-C$_4$ [23].

For dyed cotton with BFS (2), 4 major changes appeared at peaks 882.83, 1000, 1056.6, 1173.7 and 1396 cm$^{-1}$ respectively, which endorse the investigation of Basak et al. (2015) [23], Paul et al. (2013) [15] and Monteiro et al. (2014) [27]. Due the presence of inorganic salts into BFS peaks exhibited at 873, 1000 and 1176 cm$^{-1}$ for potassium chloride, sodium phosphate and magnesium chloride respectively [28, 29]. Peaks at 1056.6 correspond C-H and C-O deformation band [25] and 1396 cm$^{-1}$ was responsible for CH deformation of $-\text{CH}_2$- [26]. For BFS stronger band seen at 1028.3, 1109, 1161.6, 1323.2 and 1638.4 cm$^{-1}$ for spectra of dyed fabric (2) than Control (1) by waning over all transmittance % due to presence of tannin, flavonoid, lignin, etc (Figure 4) [27].
3.2. Color Co-ordinate Values of Dyed Specimens

Table 3 depicts the CIELAB color co-ordinates of dyed specimens.

Regarding lightness ($L^*$), the samples orders were found as $A> B> E> D> C$. Minimum $L^*$ 71.89 noticed for C i.e. maximum darkness. B, C, D and E were 4.32%, 10.97%, 9.42% and 6.44% respectively darker than A. Regarding redness ($a^*$) orders of samples were found $E> B> C> D> A$. The sample E was reddish and A was greenish amongst all. B, C, D and E samples were 26.95%, 21.66%, 16.62%, and 28.21% redder than control sample. Concerning yellowness ($b^*$) orders of samples were found $E> D> C> A> B$. Among them E showed maximum and B showed minimum yellowness. The sample C, D and F were 6.40%, 7.39% and 9.39% yellower than reference sample. But B was 2.82% bluer than A. The orders of color saturation ($c^*$) of samples were found to be $E> D> C> B> A$. E had highest and A had lowest color saturation among all samples. The Sample B, C, D and E was 0.47%, 7.97%, 8.36% and 11.36% more color saturation than untreated sample correspondingly. For hue angle ($H^\circ$) orders of samples were found $A> D> C> E> B$.

The highest hue angle for A and lowest for B was observed. The hue angle of sample B, C, D and E were 7.02%, 3.36%, 2.05% and 4.0% lower than control sample respectively.

BFS comprises of many organic and inorganic compound [27]. From maximum absorption wavelength ($\lambda_{max}= 350nm$) of UV spectra it can be presumed that the color appeared in the dyed samples is liable for flavonoids [32]. The presence of hydroxyl and carbonyl groups in the dye and cellulose structure is capable to form complex by chelating via co-ordination bond with positively charged metals. Some alteration appeared in color coordinates value for mordanted dyed specimens as compared (B, C, D, and E) with control sample (A). Hence, one molecule of metal can form a bond with two or more molecules of dye and fiber simultaneously according to their co-ordination numbers. More color saturation observed for iron mordanted samples as it has coordination number 6 and has stronger capability of dye-mordant-fiber interactions than copper, tin and alum respectively. Color saturation ($c^*$) is inversely proportional with lightness ($L^*$). Alum mordanted specimens exhibited higher $L^*$ as it block dye molecules by bonding with more with dye then fiber molecule. The alteration of yellowness and redness had followed same fashion [30, 31].

3.3. Degree of Color Levelness
The orders average color difference value of samples were found C>D>E>B>A (Table 4). Though, there was difference in average color difference value but all samples showed excellent color levelness.

Homogeneity of dye molecule distribution onto the fiber surface essentially indicates the levelness of color. The unmordanted dyed samples showed better levelness due to higher homogeneous dye spreading for dye-fiber interaction. All types of mordanted colored specimens exhibited poor levelness than control sample for simultaneous dye-mordants and fiber mordants interaction [30]. Iron has stronger coordination linkage formation capability due to having 6 coordination numbers than other metals. Iron salts can form a complex one site with the fiber and other site with the dye and hence slightly greater color difference appeared. The order of strength of coordination bond formation among dye, mordants and cotton fiber interaction is iron>copper>tin>alum which bolster accessed values [31].

3.4. Color Strength (K/S) Value

The figure 2 illustrates the effect of metallic mordants on dyed materials. The dye fixation increased due to pre-mordanting action with metallic mordants. The color strength value of samples were found C>D>E>B>A orderly. The maximum color strength 1.10 was yield for C at maximum wavelength 360nm. The K/S value of B, C, D and E samples was 26.15%, 69.23%, 58.46%, and 41.54% higher than reference sample.

Iron and copper treated samples exhibited the highest K/S values. Both these metals have excellent ability to form coordination complexes by readily chelating with the dye molecule. As the coordination numbers of copper and iron are 4 and 6 respectively, some co-ordination sites stayed vacant when they interacted with the cotton. Thus these metals can form a complex simultaneously with the cotton in one site and with the dye (tannin, flavonoids)on the other site that leads high dye uptake. In case of cotton, iron exhibited stronger fabric-mordants-dye interaction than copper [30]. Alum and tin are liable for strong binding with dye but not with fiber. They block the dye and reduce its interaction with fiber. Thus lower K/S value appeared as they form weaker co-ordination linkages with dye molecule [31].

3.5. Brightness Index Value

The figure 3 depicts the effect of metallic mordants on brightness index of the sample. Regarding brightness index value, the samples orders were found as A>B>E>D>C. The highest brightness index value was 50.58 for untreated as it involved with dye-fiber interaction only. The samples B, C, D and E showed 14.97%, 30.03%, 22.44% and 19.73% lower brightness index than control sample. All mordanted samples exhibited lower brightness index value as they strongly involved with dye-mordants-fiber interaction. Lowest value yielded 35.39 for iron as it involved with stronger cotton-mordants-dye interactions than others.

Among all mordants, alum displayed brightest appearance [32]. Tin also exhibited lighter shade but it may reduce the hand feel properties [33].

![Figure 6. Color Strength (K/S) value](image)

![Figure 7. Brightness index% value](image)

Table 4. Degree of color levelness.

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<th>Time</th>
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<th>Average ∆E</th>
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<tbody>
<tr>
<td>R-1</td>
<td>R-2</td>
<td>R-3</td>
</tr>
<tr>
<td>Batch readings</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.292</td>
<td>0.038</td>
</tr>
<tr>
<td>B</td>
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<td>0.075</td>
</tr>
<tr>
<td>C</td>
<td>0.507</td>
<td>0.363</td>
</tr>
<tr>
<td>D</td>
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<td>0.209</td>
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4. Conclusions

Promising effect of metallic mordants on colorimetric property of dyed cotton fabric was accessed employing banana floral stem sap. Dye fixation rate was increased due to pre-treatment with metallic mordants. From measured colorimetric value it is concluded that limited shade was overcome by treating with metallic mordants. Medium depth of shade was appeared for using of potassium alum, iron (II) sulphate, copper (II) sulphate, tin (II) chloride. The order of shade was appeared for using of metallic mordants. From measured absorbance at 428 nm of dye and its shade value, it is concluded that limited shade was overcome by pre-treatment with metallic mordants. Medium depth of shade was appeared for using of potassium alum, iron (II) sulphate, copper (II) sulphate, tin (II) chloride. The order of shade was appeared for using of metallic mordants. Medium depth of shade was appeared for using of potassium alum, iron (II) sulphate, copper (II) sulphate, tin (II) chloride. The order of shade was appeared for using of metallic mordants.

REFERENCES


