Research Article

FT-IR Analysis of *Beta vulgaris* Peels and Pomace Dye Extracts and Surface Analysis of Optimally Dyed-Mordanted Cellulosic Fabrics

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FT-IR spectroscopy is a nondestructive technique that can be utilized for the qualitative characterization of natural dyes and dyed substrates through structure elucidation. This work aimed at the characterization of natural dye extract from *Beta vulgaris* peels and pomaces and surface analysis of optimally dyed-mordanted cotton (cellulosic) fabric using Fourier Transform Infrared (FT-IR) spectroscopy, as well as colour fastness tests (light, washing, rubbing, and perspiration). Response surface methodology (RSM) was employed in the optimization of dyeing temperature (T), time (t), and pH, as well as applying the relative percent change in colour strength (ΔE) of dyed fabrics as the response. The natural mordants (tannic acid-alum) were compared with synthetic mordants ($K_2Cr_2O_7$, $FeSO_4$, and $CuSO_4$) using the three mordanting methods. The optimized dyeing parameters were T (55˚C), t (75 minutes), and pH (6.5), as a result of comparatively high relative % ΔE (11%). The FT-IR analysis of the extract revealed different characteristic absorption peak values for various functional groups: 3282.82 cm^{-1} (–OH stretch), 2932.96 cm^{-1} (C–H stretch), and 1588.91 cm^{-1} (C=N stretch), among others. The C=N bond stretch biomarks the presence of nitrogen-containing compounds such as the reddish betanin pigments. $p > 0.05$ of the dyeing parameters implied that they are not significant but affect dyeing probably alongside other factors such as mordanting. The spectral analysis of bleached and optimally dyed (nonmordanted and mordanted) fabrics revealed varied peaks indicating different functional groups suggesting the presence of cellulose and the binding of mordants with chromophores in the dye extract which yield different shades. Postmordanting showed mean ratings of 4-5 (excellent) among all fastness tests, displayed by tannic acid-alum, $FeSO_4$, and $CuSO_4$. Generally, mordanting resulted in enhanced dye stability and improved colour fastness. To identify specific chromophores in dye extracts and their molecular configurations due to mordants, advanced FT-IR hyphenated systems can be employed.

1. Introduction

Over the centuries up to the 19th century, organic dyes have been the main colour additives for many textile materials around the world [1, 2]. Natural dye products were regarded the most beautiful and exotic pigments reserved for those of high status [3]. The introduction of synthetic dyes in 1856, when the first commercial synthetic dye, mauve, was discovered by British chemist William H. Perkin, led to an almost complete displacement of natural dyes. This is because natural dyes exhibit poor-to-moderate wash and lightfastness, while their synthetic counterparts represent the full range of colour strength, wash, and lightfastness at relatively moderate costs [4]. Furthermore, they are found to have favorable application properties with a wide range of colors to select from, higher reproducibility within a short time, and improved quality of dyeing [5]. The interest in the use of synthetic dyes has reversed and is in rapid decline currently because of their adverse environmental effects, since they are produced from nonrenewable and nonbiodegradable petrochemicals [6]. Approximately 30 million tons of dyes are being consumed globally in textile industries

with about 70,000 tons being released to the environment annually [2]. According to the Business Week, the percentage of humans who are allergic to textile auxiliary chemicals rose to 60% by 2020 [7, 8]. In addition, costly methods are employed to eliminate synthetic dyes from the environment. On the other hand, natural dyes are easily disposable because they are biodegradable and they are obtained from renewable sources: plants, animals, and minerals [9, 10]. Furthermore, they are nonpollutants and have become an ideal choice of dyeing due to their non-toxicity, noncarcinogenicity, and ease of handling [11]. This study aimed at characterization of the colouring compound in *B. vulgaris* peels and pomaces as well as surface changes of the naturally dyed-mordanted cotton fabric by FT-IR technique.

Natural dyes require mordants or anchors to fix them on fabrics. Mordants possess an affinity for both the fibre and the dye through coordination bonding between them; hence the mordant-colour complexation increases colourant uptake attributed to the formation of charge-transfer complexes and increase in conjugation lengths [12]. Furthermore, mordants enhance the colour fastness of dyed fabrics [11, 13]. Common mordants used for dyeing are metallic mordants [5] such as $CuSO_4$, $FeSO_4$, K_2CrO_4, and $SnCl_2$, while naturally obtained mordants include $Al_2(SO_4)_3 \cdot 12H_2O$ (alum) and tannic acid [5, 14].

Several techniques of separation are employed in the characterization of the bioactive compounds in plant extracts, such as UV-Vis spectrometry, FT-IR, NMR, and mass spectrometry [15]. FT-IR is a known valuable tool for the identification and characterization of diverse functional groups present in unknown plant extracts [16, 17]. FT-IR spectra of pure compounds are usually so unique that they are sort of a molecular "fingerprint." Typical FT-IR spectra show several absorbance peaks due to fundamental transitions. They are distributed discriminately in four regions (the -OH stretching region, 4000–2500 cm^{-1}; the triple-bond region, 2500–2000 cm^{-1}; the double-bond region, 2000–1500 cm^{-1}; and the "fingerprint" region, 1500–600 cm^{-1}) [18]. The region in the IR spectrum above 1200 cm^{-1} shows spectral bands or peaks due to the vibrations of individual bonds or functional groups under examination, while the region below 1200 cm^{-1} indicates the "fingerprint region." This work aimed at characterization of natural dye extract from *Beta vulgaris* peels and pomaces and surface analysis of optimally dyed-mordanted cotton (cellulosic) fabric using Fourier Transform Infrared (FT-IR) spectroscopy, as well as colour fastness of the dyed fabrics.

2. Materials and Methods

2.1. Chemicals and Reagents. Methanol, formic acid, acetone, isopropyl alcohol, hexane, ethyl acetate, glacial acetic acid, copper (II) sulphate, potassium dichromate, tannic acid, alum, sodium hydroxide, Gulbar salt (sodium sulphate), and sodium carbonate were purchased from Loba Chemie, India; iron (II) sulphate was acquired from Blulux, India; PENETROL HPLF-E wetting agent and sodium lauryl sulphate (SLS) were obtained from Pacific Texchem, India. All the chemicals and reagents were of analytical grade and were used without further purification.

2.2. Equipment. The equipment used was Soxhlet apparatus and Whatman cellulose extraction thimbles (Sigma Aldrich, Germany); Standard Portable PX Meter (0.1 pH Resolution); rotary vacuum evaporator (Hahnvapor Rotary Evaporator HS-2005S, Korea); TLC plates-60RP-18 (Sigma Aldrich, USA); standard swatch master, spray master (with AATCC certified standard spray test rating chart), dye water bath, padding mangle, and spectra vision (5 L) colour matching booth (Paramount Instruments Pvt Ltd, India); FT-IR (Bruker Alpha, USA, equipped with Platinum ATR beam splitter, with monolithic diamond crystal); and Reference Bench-Top Spectrophotometer (SP60 *X*-Rite, USA).

2.3. Extraction and Concentration of Betalain Pigment. The fresh peels and pomace of *B. vulgaris* were sliced into small pieces, placed over a layer of wax paper, and dried in an oven at 40°C for 8–10 h until the sample was completely dry and crunchy. The dried plant material was then ground using a pestle and mortar into very fine powder. Finely sieved (2 mm pore-sized sieve) *B. vulgaris* powder (20 g) was weighed into a Whatman cellulose extraction thimble. Then methanol 200 mL was measured into a 500 mL Schlenk flask of the Soxhlet apparatus and extraction was carried out at the boiling point of methanol (65°C) for 11 h. A constant pH of 4 was maintained by applying a few drops of formic acid (this was for stability of *B. vulgaris* red colour which depends directly on its pH, the optimum pH being between 4 and 5 as reported by Antigo et al. [19]). The dye extract obtained was filtered and concentrated by a vacuum rotary evaporator to obtain 10.65 g (53.25%) of a red solid.

2.4. Thin Layer and Column Chromatography. Different combinations and ratios of several solvents (from polar to nonpolar) were mixed volume by volume and used on TLC plates to establish the best mobile phase solvent system. The polar solvents used were methanol, deionized water, acetonitrile, acetone, isopropyl alcohol, and glacial acetic acid (protic solvent), while nonpolar solvents were hexane and intermediate ethyl acetate. The best solvent system established that constituted methanol:acetic acid:distilled water at (90:7:3)% ratio, respectively, was used in column chromatography packed with silica gel (60–200 mesh) to isolate the extract. The collected liquid fractions which had the same R_f values through TLC were combined on amber vials and were then concentrated to solid awaiting further analysis.

2.5. FT-IR Analysis of B. vulgaris Peels and Pomace Dye Extracts. The concentrated fractions of *B. vulgaris* peels and pomace extract were analyzed for the functional groups present, using Fourier Transform Infrared (FT-IR) spectroscopy according to Huck [20]. Approximately 5 mg of each sample and 5 mg KBr in each sample were used. The

FT-IR spectrophotometer was operated at a spectral range of 350–$7500\,cm^{-1}$ and a resolution of $8\,cm^{-1}$. The spectra were generated by OPUS version 7.5 software and interpreted using the guidelines as described by Kumar and Su-Ling Brooks [21].

2.6. Optimization and Statistical Modelling of Dyeing Variables.

Optimization of process conditions is very important to achieve maximum response or outcome. Central composite design (CCD) is very useful for process optimization and modelling tool of response surface methodology (RSM) in the evaluation of the key effects as a result of interactions among various factors concurrently affecting that process [22–24]. To determine the maximum change of colour on cotton fabrics due to *B. vulgaris* peels and pomace dye, CCD and RSM were applied for optimization. The chosen variables that affect dyeing are dyeing temperature (T), dye bath time (t), and pH. The respective variables were denoted as A for dyeing T (oC), B for dye bath t (minutes), and C for pH of the dye bath. The five CCD levels were coded $-\alpha$, -1, 0, $+1$, and $+\alpha$. The alpha (α) value is the distance of each axial point from the center in a CCD. When the α value is less than one, the axial points are inside the cube; a value equal to one put the points on the face of the cube, while a value greater than one put them outside the cube. The $-\alpha$ and $+\alpha$ values are the lower and higher extreme values, respectively, in CCD, as the model permits the two extended level factors. The -1, 0, and $+1$ codes denote the lowest, central, and the highest level of the variables, respectively. T of $20°C$ and $90°C$, t of 30 mins and 120 mins, and pH of 4 and 9 were used as the lowest and highest values of the variables in each case, respectively (Table 1).

In the dyeing optimization, natural mordant concentration (order of tannic acid-alum) of 50% on-weight-fabric (o.w.f.), M : L ratio (1 : 20 o.w.f.), and 2 g pure cotton fabric were kept constant while employing postmordanting method. The dyed and mordanted fabrics after each experimental run were subjected to SP60 X-Rite Spectrophotometer to deduce their relative percent change in colour strength (ΔE).

In statistical modelling of the experimental design with the three factors, a model encompassing linear and quadratic terms can be expressed as the second-order polynomial equation (1). Multiple linear regression (MLR) using Microsoft (MS) Excel was performed to obtain the coefficient values.

$$\text{Response, } y = b_0 + (b_1 F_1) + (b_2 F_2) + (b_3 F_3)$$
$$+ (b_4 F_1 F_1) + (b_5 F_2 F_2) + (b_6 F_3 F_3) \quad (1)$$
$$+ (b_7 F_1 F_2) + (b_8 F_1 F_3) + (b_9 F_2 F_3),$$

where y represents the relative % ΔE, while b and F are the coefficients and factor variables, respectively.

The response surface plots were obtained through Minitab statistical process modelled through CCD to demonstrate the effects of interactions among the variables that affect dyeing and response. In this way, it is possible to obtain optimum parameters or conditions of an experiment.

TABLE 1: Experimental variables and their coded levels for dyeing.

Variables		Coded levels				
Symbol	Name	$-\alpha$	-1	0	$+1$	$+\alpha$
A	Temp. (°C)	2.155	20	55	90	112.16
B	Time (mins)	1.515	30	75	120	148.49
C	pH	2.4175	4	6.5	9	10.5825

Statistical significances of the predicted models were evaluated by ANOVA and least-squares techniques generated to determine which factors significantly affect the studied response variables. p value represents a decreasing index of the reliability of a result such that a p value less than 0.05 (typically ≤ 0.05) is statistically significant, implying that there is strong evidence against the null hypothesis.

2.7. Dyeing and Mordanting.

Desized, scoured, bleached, and mercerized 100% cotton fabrics of 98.9 GSM were used. The control measures were undyed and unmordanted cotton fabrics. The optimized dyeing conditions were used to prepare the dye bath solution for dyeing cotton fabrics of weight of 2 g, with the dye concentration of 70% on-weight-fabric (o.w.f), guided by the dyeing procedures as reported by Hong [25] in a laboratory-scale dyeing bath. Mordanting was performed separately and individually using natural mordants (order of tannic acid-alum) and metallic mordants (iron (II) sulphate, sulphate, copper (II) sulphate, and potassium dichromate) each at 50% concentration o.w.f following the three methods of mordanting: premordanting, simultaneous mordanting, and postmordanting methods [26]. To achieve maximum dye exhaustion, 20% o.w.f sodium sulphate was added to the dye bath [27]. In premordanting, the mordant was first added to a beaker containing the fixed quantity of dye solution, followed by the addition of cotton fabric samples. The whole mixture was thereafter slowly brought to boil in the water bath. After dyeing, the solution was allowed to cool, the fabric was gently removed, washed, air-dried, and stored for analysis. Simultaneous mordanting involved dyeing and mordanting at the same time, while postmordanting involved the addition of the mordant after dyeing. The mordant was added to the dye bath in the final ten to twenty minutes of simmering. The fabric was ejected out of the solution and left to cool, and normal washing was performed using 2 g/L sodium lauryl sulphate (SLS) to remove unfixed dye [28] and then finally air-drying.

2.8. FT-IR Characteristics of Dyed Cotton Fabrics.

FT-IR analyses of bleached cotton fabrics and optimally dyed and mordanted cotton fabrics were performed to observe the effects of dye and mordants on the fabrics spectroscopically. Bleached and dyed fabrics were each ground separately to a fine powder and approximately 5 mg of each sample was collected on the Alpha Bruker Optic instrument and analyzed separately. Approximately 5 mg KBr in each sample was used and the FT-IR operated at a spectral range of 350–$7500\,cm^{-1}$ with $8\,cm^{-1}$ resolution. The spectra
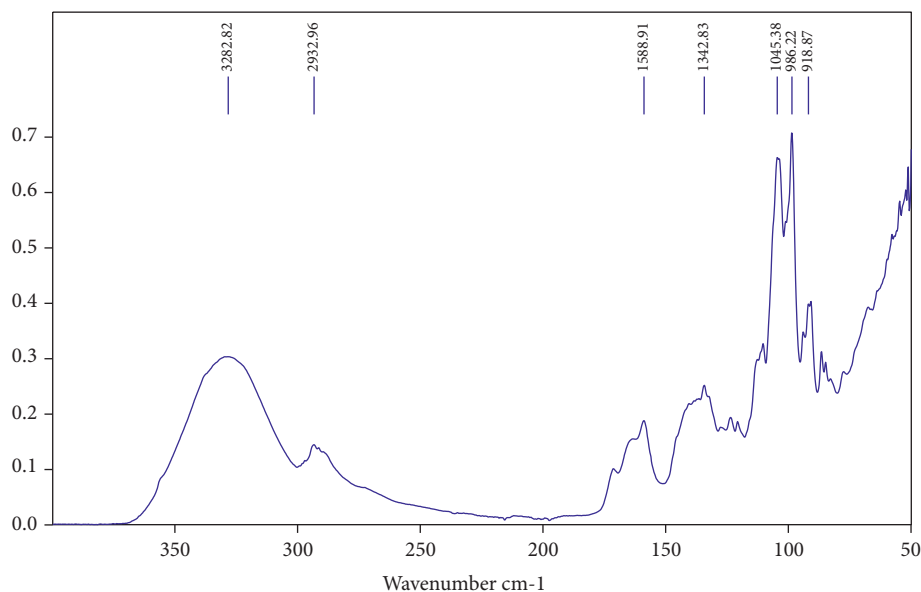
FIGURE 1: FT-IR spectrum of *B. vulgaris* peels and pomace extracts.

generated were interpreted according to Kumar and Su-Ling Brooks [21] with the help of OPUS version 7.5 software.

2.9. Colour Fastness Properties Tests. The preconditioned fabrics' colour fastness tests were evaluated according to ISO/AATCC standards and procedures which are ISO 105-C-06 : 2010 (E) for colour fastness to domestic and commercial laundering (washing); ISO 105 Part X12 for colour fastness to rubbing (wet and dry); and ISO 105-B02 for colour fastness to artificial light: MBTL fading lamp test and ISO 105 E04 for perspiration fastness (acid and alkaline). The standard reference samples and dyed cotton samples were then assessed using grey scales for colour change and staining, according to ISO/AATCC standard methods.

3. Results and Discussion

3.1. FT-IR Analysis of B. vulgaris Peels and Pomace Dye. Figure 1 shows the FT-IR spectrum of *B. vulgaris* peels and pomace isolate. The band at 3282.82 cm^{-1} is attributed to the stretching vibration of the –OH bond due to hydroxyl groups [29]. The band at 2932.96 cm^{-1} is attributed to the vibrational stretching of the C–H bond due to alkanes [30], while the band at 1588.91 cm^{-1} is assigned to the extension stretching vibration of the C=N bond. The C=N bond is the aldimine bond that binds the betalamic acid in the dopa cycle. The presence of these nitrogen-containing functional groups indicates the presence of betalains in the peels and pomace of *B. vulgaris* as they are *N*-containing compounds. The results of the present study are in agreement with the findings of Kumar et al. [29] in the study of extraction, optimization, and characterization of water-soluble red-purple pigment from floral bracts of *Bougainvillea glabra*. The –OH and C–H peaks indicate the presence of hydroxyl groups from alcohols, as well as different types of carbohydrates such as lignin, cellulose, hemicelluloses, and pectin

[31]. The band at 1342.83 cm^{-1} corresponds to the C–H aliphatic bending of the organic compounds in the extract [30]. The band at 1045.38 cm^{-1} is assigned to the symmetric stretching vibration of the C–O–C link [32]. This linkage suggests that *B. vulgaris* peels and pomace also contain polysaccharides such as sugars and pectins [31]. On the other hand, the band at 986.22 cm^{-1} is responsible for the bond deformation of the C–H bond and the aromatic C–H in-plane bending, and the band at 918.87 cm^{-1} corresponds to the stretching vibrations of the C–COOH bond for carboxylic acids [33].

The vibrational and electronic properties of different molecules are related to the molecular configuration and influence each other through vibronic coupling. Vibronic coupling predicts the visible absorption spectra and colour of biomolecules, including those of many biological pigments such as betanins, flavins, carotenoids, and anthraquinones [34, 35].

3.2. Dyeing Optimization and Statistical Model. The respective relative % ΔE (Table 2) that were positioned as the response (y) and regressed alongside the independent variables by fitting onto equation (1) led to the formation of equation (2). The two out-of-range values (-2.155 and 112.155) in Table 2 signify the lower and higher extreme values of temperature, respectively.

$$y = 5.59 + 0.0013A + 0.0239B - 0.033C. \qquad (2)$$

The regressed variables by way of ANOVA are demonstrated in Table 3. The p values of the variables were greater than the common α level of 0.05, which indicated that they were not statistically significant. This means other factors such as mordants and their concentrations could have also affected dyeing and subsequently the relative % ΔE. Therefore, it necessitated the use of mordants to fix and modify the colour on fabrics according to Konar and

TABLE 2: Experiments planned in CCD for dyeing optimization and response (y).

Run order	Temp. (°C)	Time (min)	pH	Response, y (relative % ΔE)
1	55	75	6.5	11.0
2	−2.155	75	6.5	5.1
3	112.155	75	6.5	7.1
4	55	148.485	6.5	5.4
5	55	1.515	6.5	3.9
6	55	75	10.5825	8.2
7	55	75	2.4175	10.3
8	90	30	4	6.7
9	20	30	9	6.0
10	90	120	9	7.1
11	55	75	6.5	9.5
12	90	120	4	8.9
13	20	120	9	7.6
14	90	30	9	7.2
15	20	120	4	5.3
16	20	30	4	7.0

TABLE 3: ANOVA for dyeing process.

Properties	df	SS	MS	F	Significance F	p value
Intercept	3	5.74209	1.9140	0.4833	0.69962	0.01026
Temp., °C	13	51.4885	3.9607			0.60370
Time, mins	16	57.2306				0.29970
pH						0.99684
Regression statistics						
Multiple R	0.316753					
R [2]	0.100333					
Adjusted R^2	−0.10728					
Standard error	1.990139					

Samantha [5] and Kulkarni et al. [13]. The p value of the intercept is less than the significance level of 0.05; hence, the model fitted the data well. Similarly, the R^2 value of 0.100333 (>0) was also an indicator of good fitness of the model.

The response surface plots represented in Figures 2(a)–2(c) were employed to examine the correlational effects of variables (dyeing temperature, pH, and time) on the response (relative % ΔE). The investigated variables have some effect on dyeing in terms of linear, quadratic, and cross-terms leading to optimized dyeing conditions of T of 55°C, t of 75 mins, and pH of 6.5. It was established that the response y that was relatively high was taken as the best condition favouring optimum dyeing as observed in the surface plots. Increase in dye bath concentration leads to more dye transfer to the fabric and hence a higher apparent depth of colour [36].

The significance of the quadratic terms in equation (2) indicates that the dyeing variables (dyeing temperature, pH, and time) have some impact on dyeing efficiency, even though their effects on the relative % ΔE were less significant. As seen in Figures 2(a)–2(c), the effects of interactions among time, pH, and temperature on colour compounds are demonstrated. When the temperature is maintained at a constant level (Figure 2(a)), the increase in time and decrease in pH lead to increased dye absorption. The highest dyeing efficiency of cotton fabrics cannot be achieved at a low time and high pH.

In Figure 2(b), when pH is maintained as a constant, a slight increase in time (50–100 mins) leads to more percent dye intake but high temperature (>80°C) can denature the coloured compounds, such as betalains, leading to low dye uptake by cotton fabrics resulting in poor dyeing. Many phytochemicals are denatured by high operation time and temperature as reported by Ravichandran et al. [37]. Moderate temperature favours the stability of compounds such as betanin pigment, hence unlimited absorption onto cotton fabrics. The thermal stability correlation can be explained by the findings of Gokhale and Lele [38] who investigated the impact of hot air on *B. vulgaris* colour compounds. In Figure 2(c), when time remains constant, moderate temperatures (40–80°C) and low pH (4–7) favour optimum dyeing. At very high pH and high temperature, betalains are destroyed and chromophoric effect is lost [37].

3.3. *Characteristics of Dyed Cotton Fabrics.* The mordanted *B. vulgaris* peels and pomace dyed cotton fabrics depicted varied shades under the different mordants applied. They were deeper than unmordanted dyed fabrics as can be seen in Table 4. A deeper shade is seen in postmordanted dyed fabrics, unlike premordanted dyed fabrics that have the lightest shades among all mordanted dyed cotton fabrics, confirming Bukhari et al.'s [39] findings, in dyeing and fastness properties studies of brown naphthoquinone

Surface plot of relative % ΔE vs pH and Time (mins)

(a)

Surface plot of relative % ΔE vs Temp. (°C) and Time (mins)

(b)

Surface plot of relative % ΔE vs pH and Temp. (°C)
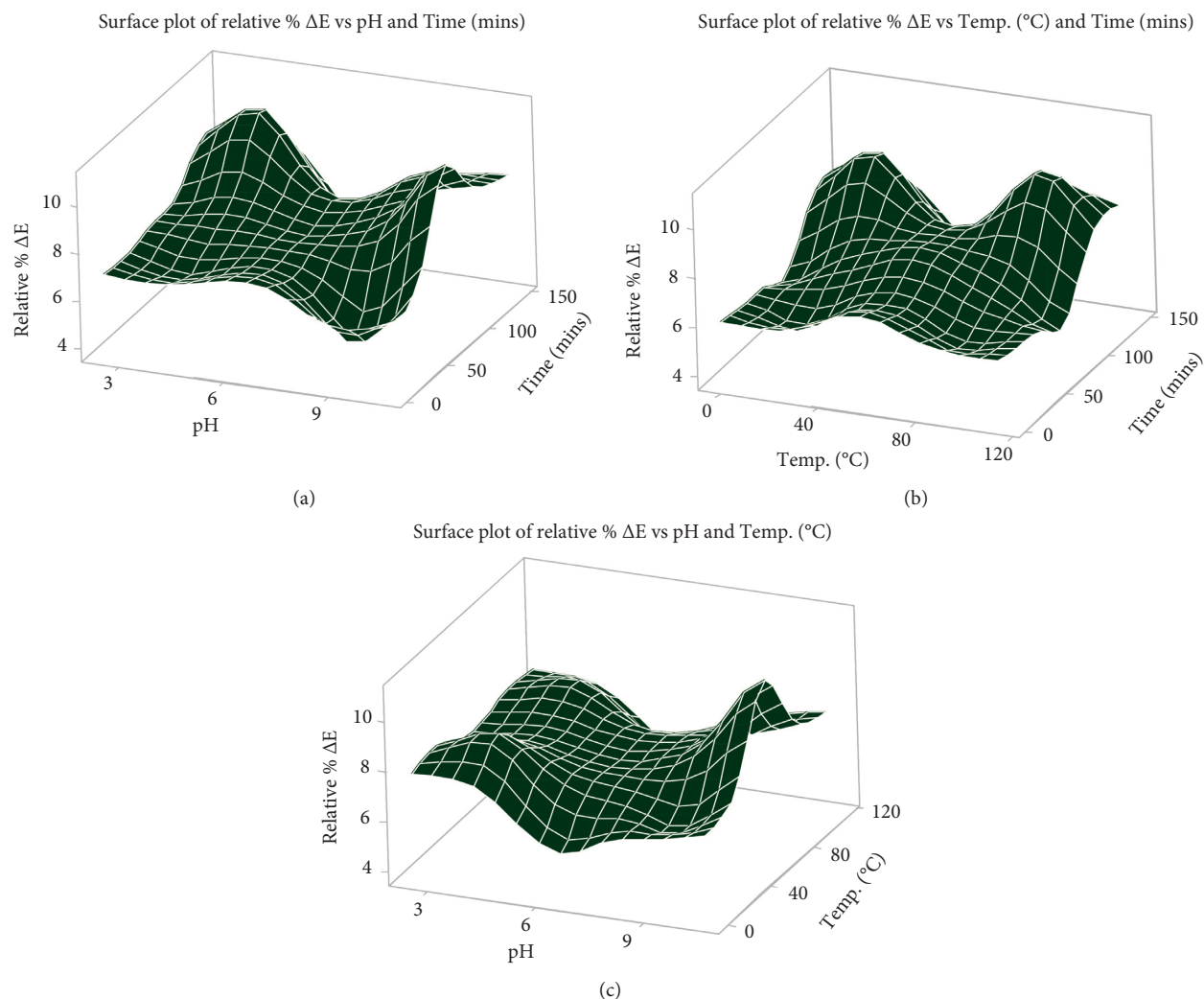

(c)

Figure 2: RSM for dyeing of the cotton substrate using *B vulgaris* peels and pomace extract. (a) Correlational effect of pH and time on relative % ΔE. (b) Correlational effect of temperature and time on relative % ΔE. (c) Correlational effect of pH and temperature on relative % ΔE.
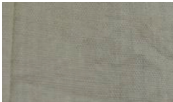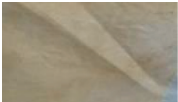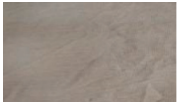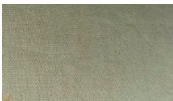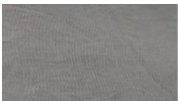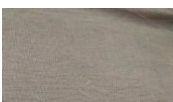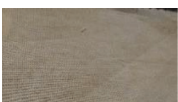
colourant dye extracted from *Juglans regia* L. on natural wool fibre while using different metal salt mordants.

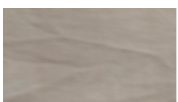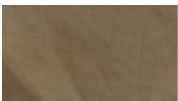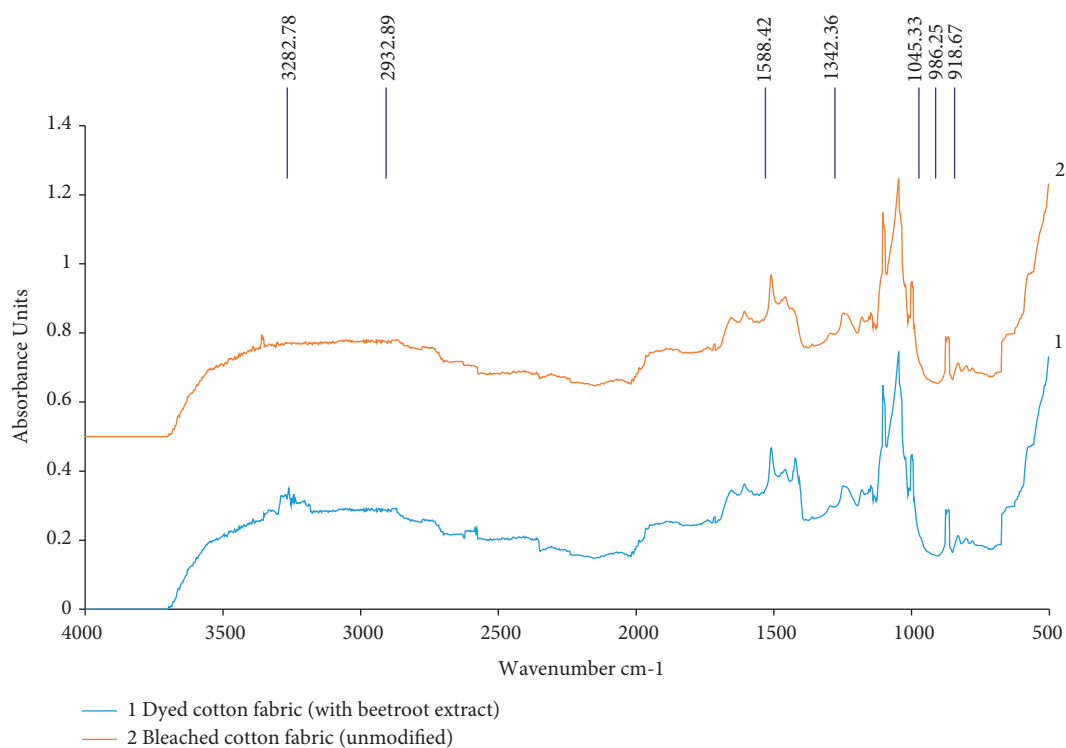The tannic acid-alum and FeSO₄ mordanted dyed fabrics are outstanding in the depth of shade compared to their corresponding CuSO₄ and K₂Cr₂O₄ dyed cellulosic fabrics. Alum and chrome belong to the group of brightening mordants. They usually produce pale versions of the dye colour in consideration. The tannic acid-alum mordanted fabric appears in the same hue but deeper shade as the *B. vulgaris* peels and pomace dye extract. Tannin that has a high affinity for cellulose is normally mixed with alum to help in the bonding process. Aluminum in alum has a valence of three (Al^{+3}), demonstrating a possibility that three molecules of dye are attached to each atom of the mordant metal (Al) resulting in deeper and brighter staining characteristics [40]. Consequentially, there is higher reactivity of Al^{3+} towards hydroxyl functional groups (OH) of cellulosic substrate that accelerates the diffusion of dye molecule into the fabric matrix [8]. *B. vulgaris* peels and pomace extracts

are highly stable in mild acidic media and this explains the persistent deeper shades in tannic acid-alum mordants. FeSO₄ and CuSO₄ belong to the group of dulling mordants [5]; hence, they produce dull shades with shifted hue and depth from the dye in consideration. Due to their +2 valencies (Fe^{2+} and Cu^{2+}), two molecules of the natural dye are bonded to each atom of the mordant metal (Fe and Cu) resulting in dull shades [40].

3.4. FT-IR Characterization of Dyed and Mordanted Cotton Fabrics. The bleached and optimally dyed-mordanted cotton fabrics were analyzed by FT-IR spectroscopy to ascertain structural changes due to the dye and mordants effects. Spectra (1) and (2) in Figure 3 show the *B. vulgaris* peels and pomace dyed nonmordanted and bleached cotton fabric, respectively. There are two significant changes resulting in an increase in peak intensity at $3282.78 \, cm^{-1}$ and $1588.42 \, cm^{-1}$ for the spectrum of the dyed nonmordanted

TABLE 4: Effect of mordants on shades of *B. vulgaris* dye extract.

Mordant	Pre	Mordanting method Simultaneous	Post
Without mordant			
Copper sulphate			
Ferrous sulphate			
P. dichromate			
Tannic acid-alum			

FIGURE 3: FT-IR spectra of cotton fabric dyed with *B. vulgaris* extract (1) and unmodified (bleached) cotton fabric (2).

fabric (spectrum 1) compared to the bleached fabric (spectrum 2). The changes are attributed to the increase in the number of the functional groups associated with the −OH molecular bond leading to its stretching vibration (OH wagging in phenolic compounds) as suggested by Kumar et al. [29]. The −OH group participates in bonding during the dyeing process; hence, change in peaks is expected. There is no visible change in the position of the CH_2 peaks at $2932.89 \, cm^{-1}$, and that is to be expected since this functional group does not participate in bonding during dyeing. These
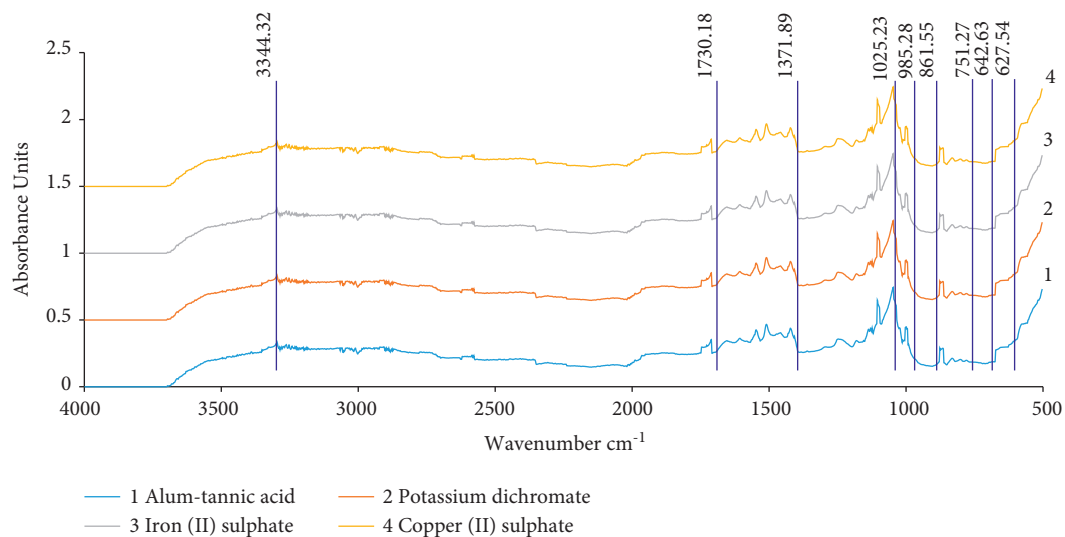
FIGURE 4: FT-IR spectra of the optimally dyed cotton fabric modified with natural mordant (1) and metallic mordants (2, 3, and 4).
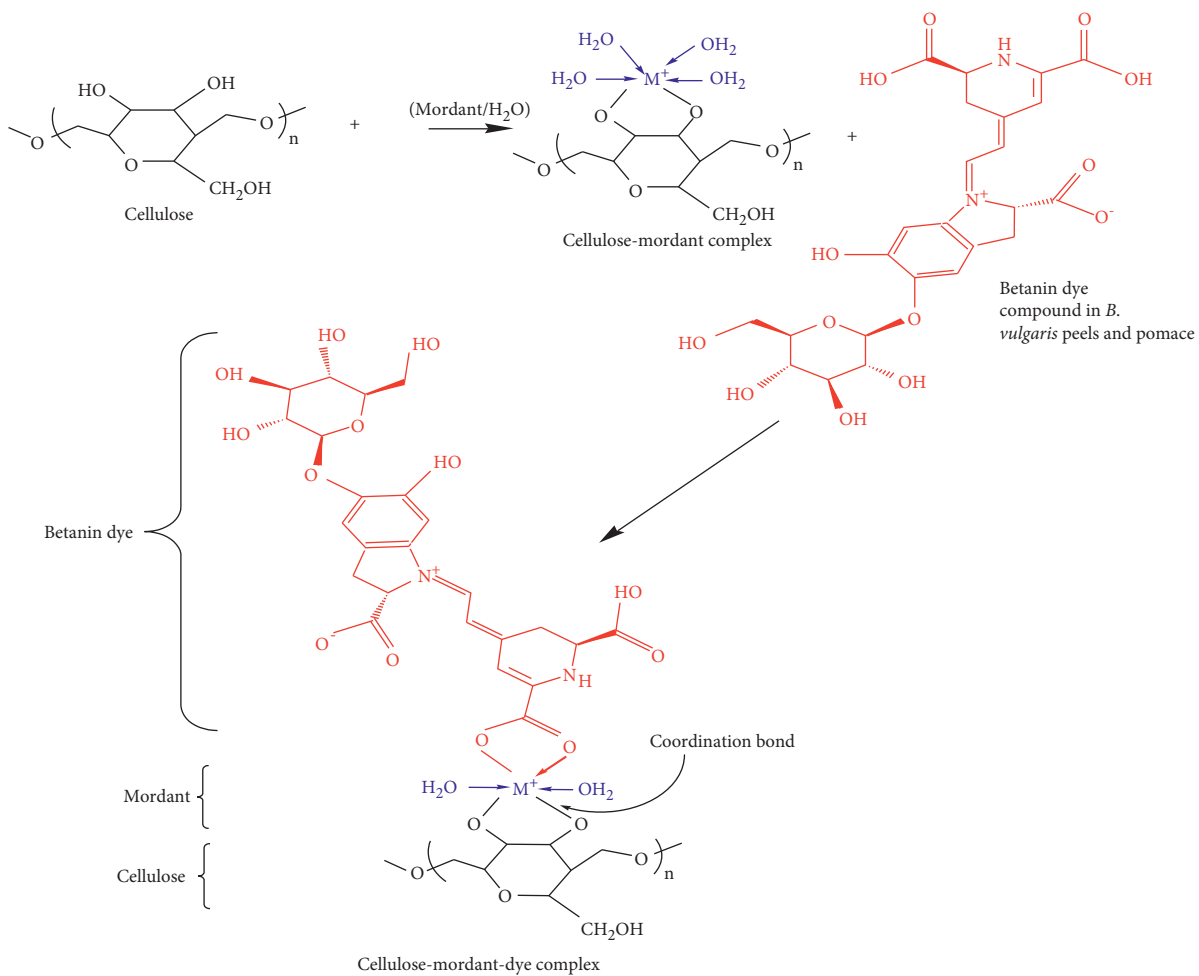

FIGURE 5: A plausible interaction of cotton fibre-mordant-betanin dye complex. M represents the metal ion from the mordant.

TABLE 5: Colour fastness rating to colour change and staining.

Mordant	Method	Washing is 105-C06 : 2010		Rubbing is 105-D02 : 2000				Light is 105-B02 : 2000		Perspiration is 105-E04 : 2000			
				Dry		Wet				Acid		Alkaline	
		C	S	C	S	C	S	C	S	C	S	C	S
CuSO$_4$	Premordanting	3/4	3/4	4/5	4	3/4	3/4	4	4	4	4	4	4
	Simultaneous mordanting	4	4	5	4	4	4	4	4	4/5	4	4	4
	Postmordanting	4	4/5	5	4/5	3	4/5	4	4/5	4	4/5	4	4/5
FeSO$_4$	Premordanting	4	4/5	4	4/5	4	4	4	4	4	4/5	4	4/5
	Simultaneous mordanting	4/5	4	4/5	4	4	4	4/5	4	4/5	4	4	4
	Postmordanting	3/4	4/5	4	4/5	3/4	4	4	4/5	4	4/5	4	4/5
K$_2$Cr$_2$O$_4$	Premordanting	3	3/4	4	3/4	4	3/4	4	4	4	3/4	3/4	4
	Simultaneous mordanting	3/4	4	4	4	4	4	4	4	4	4	3/4	4
	Postmordanting	4	4	4	4	3/4	4	4	4	3/4	4	4	4
Tannic acid-alum	Premordanting	3/4	4	4	4	4	4	4	4	4/5	4	4	4
	Simultaneous mordanting	4	4	4	4/5	4	4	4/5	5	5	4/5	4	5
	Postmordanting	4/5	4	5	5	4	4	4/5	5	4/5	4/5	4	4
Nonmordanted		3	2/3	3	3/4	3	3/4	4	4	4	3/4	3	3/4

C is colour change; S is staining.

findings also confirm the investigations of Basak et al. [41] and de Assis et al. [33], respectively, who found similar OH wagging in cellulosic and banana fibres, respectively, after their surface modifications.

A signal at $1624\,cm^{-1}$ is associated with the substantial extension of the aldimine bond that is part of the betanin molecule not identified. The band at $1588.42\,cm^{-1}$ could be due to the extension stretching vibration of the C=N bond which is aldimine bond that binds the betalamic acid with the dopa cycle in *B. vulgaris* peels and pomace dye extract on the cotton fabric. The C–H wagging of lignin and carbohydrate in the fabric and dye sample is responsible for the peak at $1342\,cm^{-1}$ which has not shown any change [21]. The stretching of betanin hexagonal rings and the C–C bonds within the rings give rise to bands at $1045.33\,cm^{-1}$, $986.25\,cm^{-1}$, and $918.67\,cm^{-1}$ with sharp peaks possibly due to the presence of cellulose, hemicellulose, and lignin [42].

Figure 4 represents the IR spectra of dyed specimens after mordanting process. Peaks at 1371.89, 1025.23, and $985.28\,cm^{-1}$ corresponding to –C–H bend (CH and aromatic vibrations), C–O–C deformation band (symmetric and asymmetric stretch due to primary and secondary alcohols), and stretching vibration of CH_2, respectively, may be due to methanol solvent, respectively [33], occurring as a result of linkages between the dye, mordant, and cotton fabric.

Mordanting can cause a spectral shift of diagnostic bands at the natural dye due to vibronic coupling, degree of chemical interaction, and changes in electron delocalization between the cotton fabric, mordant, and dye complex [43]. There is a reduced intensity and shift of peak to longer wavelengths at $3344.32\,cm^{-1}$ band due to OH stretching as mordant combined with cellulose probably due to the presence of water and salts used in wet-processes [44]. The coordination of the dye to the metal in mordants resulted in the elimination of H in the OH group, hence the subsequent decrease in peak intensity.

Figure 5 demonstrates a possible interaction of the dye, the fabric, and the mordant. Cellulose reacts first with mordants as they have a strong affinity to each other and consequently with the dye as mordant is attracted to the dye [40]. Mordants enhance the ionic interaction between the carboxylate anion of the betanin dye and cotton fibres. Betanins are nitrogenous pigments and betalamic acid derivatives. The pigmentation of betanin is associated with the resonance of the electrons cloud of the conjugated double-bond system in its structure entailing *cyclo*-L-3,4-dihydroxyphenylalanine (*cyclo*-dopa). This part of the structure of betanin is the chromophore, responsible for its characteristic absorption (532–550 nm) and red-violet pigmentation. Betanins also contain hydroxyl groups (–OH) in their structures which render them highly hydrophilic. These groups lead to charge polarization and the subsequent coordination bond formation.

3.5. Colour Fastness Properties Tests. In this experimental study, we have shown that different techniques of mordanting change the shades or enhance colour. The wash fastness results of all samples were found to be in the range of moderate-to-fairly good ratings of 3-4/5 in all the mordants. In Table 5, colour fastness to laundering in the premordanting method was fair especially for $CuSO_4$ and $K_2Cr_2O_4$ with values of 3/4 and 3, respectively. However, the postmordanting method in tannic acid-alum and $FeSO_4$ positively affected the colour change with no staining in wash fastness results ranging from 4 to 4/5, which is very good to excellent. This coincides with reported colour change ratings in wash fastness of dyed-mordant cotton fabrics, ratings which vary depending on mordant [45]. Staining ratings due to unfixed dye also range from 4-5 to 2 meaning slight change to no change, while 2 means visible change on the gray scale of colour change [45]. The highest

staining of cotton fabrics is because the unfixed dyes or surface excess effect causes a lot of staining. According to Wangatia et al. [46], the greatest retention of colour in the fabric after washing was obtained when appropriate mordant was used on the dyed fabrics.

Colour fastness with respect to dry rubbing was very good for all the samples with results within 4-5. Dry rubbing postmordanted with tannic acid-alum had excellent outstanding results of 5. It was found that assessment result for colour change and staining due to rubbing was very good in simultaneous mordanting technique for $CuSO_4$ and $FeSO_4$ mordants in all the fastness tests with values ranging from 4 to 5.

The lowest nonmordanted fabric was 2/3 value, while the highest mordanted had 5. This was true for all mordanting techniques except premordanting of $CuSO_4$, $FeSO_4$, and $K_2Cr_2O_4$ mordants with respect to their lightfastness for colour change and staining, as well as acid perspiration colour change. In addition, tannic acid-alum mordants also exhibited no observable change at premordanting with respect to light fastness for colour change and staining. The outlined findings were further consistent in simultaneous mordanting; $CuSO_4$ mordant exhibited no change at light fastness for colour change and staining; $K_2Cr_2O_4$ mordant displayed no observable difference at light fastness for colour change and staining, as well as acid perspiration, while $FeSO_4$ exhibited similar results at light fastness for staining.

Furthermore, the statement was consistent in the postmordanting method for both $CuSO_4$ and $FeSO_4$ mordants at light fastness for colour change and acid perspiration for colour change, again consistent in $K_2Cr_2O_4$ mordants with respect to colour change and staining in lightfastness. The mordants on the fabric surface led to a complex interaction between compounds in *B. vulgaris* peels and pomace dye extract and metal ions that prevented the possible photochemical oxidation of the extract in sunlight.

The medium resistance to perspiration by all the three mordanting techniques was attributed to the fabric construction. This was a low GSM fabric with a plain weave unlike heavily constructed fabrics like twill and plied fabrics in which light fabrics allow enough time and space for alkali and acid to react with the fabric's colour for a long time [47].

Generally, postmordanted cotton fabrics demonstrated better fastness results among wash, light, rubbing, and perspiration fastness as seen in tannic acid-alum, $FeSO_4$, and $CuSO_4$ with mean ratings of 4-5 in colour change and staining gray scale. Postmordanting technique for tannic acid-alum posted the best results in both colour change and staining with values in the range of 4/5-5 meaning very good to outstanding. Besides, simultaneous mordanting of tannic acid-alum gave low rating in colour change and staining as compared to postmordanting. This is associated with the neutrality of the solution because of the alkaline medium. All these findings corroborate those of Sufian et al. [48] in the comparative study of fastness properties and colour absorbance criteria of conventional and AVITERA reactive dyeing on cotton fabric. The metallic salt mordants possess special properties of chelating dye molecules to form a complex in dyed fabric via hydrogen bonding [49] (Sarhan and Salem). Thus, the mordanted dyed fabrics have increased dye exhaustion and higher fastness properties ratings than unmordanted fabric [50].

4. Conclusion

The FT-IR spectra provide novel phytochemical markers from the different absorption bands characteristic of functional groups in *B. vulgaris* peels and pomace. The stretching of –OH, C–H, and C–O–C bonds is attributed to the presence of hydroxyl groups from alcohols and different types of carbohydrates such as lignin, cellulose, hemicelluloses, and pectin, as well as polysaccharides (sugars and pectins), respectively, in the *B. vulgaris* peels and pomace extract. Furthermore, the C=N bond stretch is due to the presence of nitrogen-containing functional groups, and this is ascribed to molecules such as betanin, the compound responsible for the red colour in *B. vulgaris* peels and pomace. Thus, the *B. vulgaris* peels and pomace have the potential to be utilized as cost-effective dyeing material, and this can serve as a more sustainable option to solve the waste disposal problem. Additionally, the FT-IR spectra of the dyed-mordanted cotton fabrics showed some slight changes in the intensity of peaks as compared to bleached fabrics, which is attributed to the cotton surface modification by the dye and mordants. Optimization of dyeing conditions is critical to minimize the cost and time of dyeing process, as well as to realize the best quality of the dyed fabric in terms of relative percent change in colour strength. The large p values ($p > 0.05$) of the dyeing parameters (dyeing temperature, time, and pH) implied that they are not significant but affect dyeing as observed in the response surface plots. This means other factors such as mordants and their concentrations have some effect on colour characteristics of cotton fabric and subsequently the relative % ΔE. The dyed fabric significantly withstood colour fastness to washing, rubbing, artificial light, and perspiration due to mordanting. Natural mordants (tannic acid-alum) demonstrated a similar capacity to modify the surface of cotton fabrics in fixing the potential *B. vulgaris* peels and pomace extract natural dye just like their synthetic counterparts. To identify and quantify specific chromophores in dye extracts and conduct a qualitative analysis of molecular configurations due to specific mordants, futuristic IR hyphenated systems can be employed.

Data Availability

The data that support the findings of this study have been deposited in the Moi University repository (http://ir.mu.ac.ke:8080/xmlui/handle/123456789/5622).

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgments

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