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Green production of simultaneous coloration and functional finishing on hemp textiles through dyeing with *Diospyros mollis Griff.* extract

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Abstract

Nowadays, there is a rise in the production of eco-friendly, value-added textiles from natural substances. Some plant extracts can simultaneously dye and impart functionalities to textile fibers. The main goal of this study was the development of anti-UV and antibacterial hemp fabrics through dyeing with aqueous extracts obtained from *Diospyros mollis Griff.* Fruits without using any hazardous chemicals. Response surface methodology (RSM) was used to optimize the dyeing process and evaluate parameter interactions. The optimal pH, dyeing concentration, dyeing temperature, and mordant concentration were 4, 200 %owf, 92°C, and 5.4 %owf, respectively. The dyed fabrics were evaluated for coloration properties (color strength and fastness properties) as well as functional properties (ultraviolet protection factor (UPF) and antibacterial activity).The resulting fabrics appeared black, and displayed satisfactory color strength along with satisfactory color fastness (ratings > 4). The dyed fabrics exhibited good antibacterial activity against both *S.aureus* and *E.coli* (bacterial colony reduction > 90%), however it was more pronounced against *E.coli*. The UPF of the dyed fabrics also achieved the maximum (40+) level, highlighting the excellent UV shielding property. Thus, *Diospyros mollis Griff.* fruit extract could be a new source of a natural black dye and functionalization agents for UV-protective and antimicrobial textile applications.

1. Introduction

Synthetic dyes are commonly used to dye textiles due to their low cost and rich colors. However, the synthesis of chemical dyes and their application to textiles cause effluents that are hazardous to the water system. In addition, many types of chemical intermediates and toxic solvents used in synthetic dyes for better bindings can harm living beings through serious pollution. Natural dyes are non-toxic and environmentally friendly, and they have been gaining popularity to replace synthetic dyes in textile industry. Most natural dyes contain bioactive phytoconstituents that can be used to create bioactive fibers with antioxidant, antimicrobial, and UV-protective properties in addition to their distinctive hues and tones. [1-7]. Despite their benefits, natural dyes have some disadvantages, such as poor color fastness and a limited shade range on textiles. Metal salt mordants are frequently used to overcome the problems by improving the dye's affinity for textile fibers. However, using metal mordants can significantly alter the fiber's final color and can harm the environment by releasing heavy metal ions into the dye effluent [8]. Consequently, the replacement of typical metal ions with bio-mordants is a crucial aspect in the development of natural textile dyeing [1,4,9]. Tannin as a bio-mordant is utilized in textile dyeing as a colorant compound and a bio-mordant to increase the uptake of the dyes and improve their fastness properties. Multiple phenolic hydroxyl groups in tannin lead to the formation of complexes with proteins, metal ions, and other macromolecules such as polysaccharides [1]. Tannin can be divided into two types based on its chemical structure: condensed tannin and hydrolyzable tannin. Tannic acid is one of the simple and special forms of hydrolyzable tannin. When tannic acid is used as a mordant, natural dyes bind to fibers more effectively, enhancing the quality of the dyeing process [10].

The increasing expansion of value-added textiles and apparel has generated numerous opportunities for the use of natural colorants to impart varied functional finishes. UV protection and antibacterial properties on textile substrates have a considerable impact on the international market due to consumer demands for a healthy and hygienic lifestyle [11,12]. Then, the use of natural dyes to impart UV protection and antimicrobial properties on textiles has been studied and reported in the literature [13-17]. *Diospyros mollis Griff.*, known as the "Ebony Tree" and designated as a provincial tree in Suphanburi Province, Thailand, is a shrub tree and is distributed mainly in Southeast Asian countries. In Thai traditional medicine, this plant has been used for purging intestinal parasites, nausea, emaciation, nausea and vomiting, and wasting due to chronic illnesses [18]. In addition, the extract of the *Diospyros mollis Griff.* fruits has long been used as a traditional black dye for silks and an anthelmintic medicine. Fresh fruit of *Diospyros mollis Griff.* is a rich source of diospyrol, which is a polyhydroxybinaphthyl compound as shown in Figure 1. Polyphenolic substances, flavones, flavonoids, and tannins from plants have been

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shown to absorb visible light and UVB, and can reduce their transmission through the substrates [3]. Diospyrol is highly sensitive to air oxidation, and as a result, it turns black when exposed to air. The formation of the black colorant is assumed to involve polymerization due to phenol radical coupling, quinone-phenol rearrangement, and the formation of a charge-transfer complex involving phenols and quinones [18-20]. In fact, natural dye extracts rich in naphthoquinones possess antimicrobial properties. There is few scientific study on application of diospyrol as a natural black colorant for textiles. Phuong *et al*. [19] examined the dye extraction of *Diospyros mollis Griff.* using a variety of solvents and the extract was then used to color silk fabrics. To the best of our knowledge, the extract of *Diospyros mollis Griff.* fruits has not been investigated as a natural dye for cellulose fibers and as a functionalization agent for UV-protective and antimicrobial textile applications.

Although cotton is the most popular cellulosic fabric, the climate of Thailand and other Southeast Asian countries is not conducive to its commercial production. Hemp (Cannabis sativa), which offers sustainability and economic value, was recently designated as an industrial crop in Thailand and can be grown in the northern region. Hemp fiber is composed of 57.01% cellulose, 17.84% hemicellulose, 7.32% lignin, 5.80% pectin, 1.96% ester wax, 10.09% water-soluble substance, and a trace amount of ash [5,21]. The presence of cellulosic substances in hemp fibers offers characteristics such as good water absorption, comfort, and stability. To encourage the use of hemp fabrics in high-added value products, the color yield and functional properties must be improved. Therefore, the purpose of our study was to explore *Diospyros mollis Griff.* as a source of a natural black dye and multifunctional agent (UV protection and antibacterial properties) for hemp fibers. In addition, modeling and optimization of operating parameters were investigated to improve the performance of this dyeing process. Traditionally, the optimization of textile dyeing processes has been performed by observing the impact of one factor on response output in the absence of changes to other factors (one-factor-at-a-time methodology). However, in textile dyeing processes, the effect of one process variable is dependent on the other variables, and interactions between factors must be considered. Therefore, the effects of important dyeing process factors (pH, dyeing concentration, temperature, and mordant concentration) on the color strength (*K/S*) of the dyed hemp fabrics will be investigated using RSM and Box-Behnken design (BBD) [22]. RSM has been extensively utilized to optimize the extraction process of natural dyes from a variety of sources [23-26]. In addition, there are studies that demonstrate the advantages of using RSM to optimize variables in the textile dying process, but these studies have focused on the dyeing cotton, wool, silk, and some synthetic textiles [27-29]. To validate the optimal conditions identified by RSM in practice, performance evaluations were conducted, including color fastness properties, UV protection, and antibacterial activity following AATCC, AS/NZS, and ISO Test Method standards. The goals of this study are: (1) to promote the usage of *Diospyros mollis Griff.* in textile dyeing through scientific approach; (2) to improve dye crafts by bio-mordant; and (3) to investigate a black colorant derived from a traditional Thai dye plant on hemp fibers, a new commercial crop in Southeast Asia.

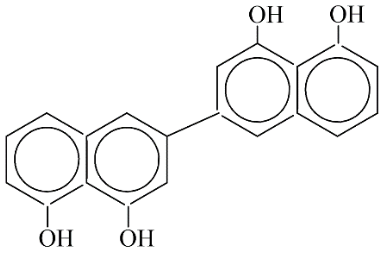

Figure 1. Chemical structure of diospyrol.

Figure 2. The aqueous extract of *Diospyros mollis Grifff.* Fruits.

2. Materials and methods

2.1 Materials

Plain weave hemp fabric (mass per unit area: 155 g·m^{-2}, warp and weft densities: 85 ends/inch, and 75 picks/inch) was obtained from a local market in Chiang Mai Province, Thailand. The fabric was scoured using 4 g·L^{-1} nonionic detergent at 70°C for 30 min to remove the dirt and impurities from the fabric. Dried berries of *Diospyros mollis Griff.* were obtained from Suphanburi Province, Thailand. Tannic acid ($C_{76}H_{52}O_{46}$), sodium hydroxide (NaOH), and hydrochloric acid (HCl) of analytical grade were bought from Sigma-Aldrich (Thailand) Company Limited.

2.2 Methods

2.2.1 Aqueous extraction of dye

Firstly, the dried berries of *Diospyros mollis Griff.* were washed thoroughly and sun-dried before use. The dried berries were ground to make a dye powder. To extract the dye, 100 g of the dye powder in 1 L of DI water were refluxed for 15 min and heated at 100°C for 2 h. Solid residues were removed by filtration, and the solution concentration was adjusted to 10 wt% and had a pH 3.85.

2.2.2 Pre-mordanting and dyeing of hemp fabrics

There are three conventional mordanting methods: pre-mordanting, meta-mordanting, and post-mordanting. The pre-mordanting is the most popular and frequently yields the best results [8]. According to the obtained results from our preliminary experiments, the pre-mordanting method was used in this study. Tannic acid was used as a bio-mordant for pre-mordanting scoured hemp fabrics before dyeing with natural dye. The exhaust method was used for pre-mordanting and dyeing of hemp fabrics. During the pre-mordanting process,

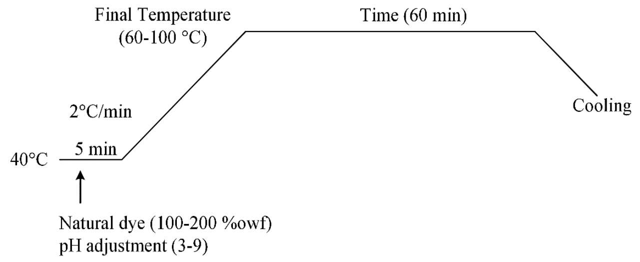

Figure 3. Schematic diagram of dyeing procedure.

the hemp fabrics were treated with different amount of tannic acid, as stated by the experimental design (1% to 8% on weight of fabric, owf) at 70°C for 60 min. After that, the treated fabrics were washed with cold water and dried at room temperature. The mordanted hemp fabircs were then dyed under conditions according to the experimental design (Table 2) following the procedure presented in Figure 3. After that, the dyed samples were then washed with 2 $g \cdot L^{-1}$ of the 1993 AATCC Standard Reference Detergent without optical brightener at 60°C for 15 min to remove excess and unfixed dyes, followed by repeated water washing, and then dried at room temperature. Both pre-mordanting and dyeing processes were carried out by keeping material to liquor ratio of 1:30 in an infrared dyeing machine (Starlet DL-6000).

2.2.3 UV-visible spectroscopy

The UV-visible spectral of the natural dye extracted from Diospyros mollis Grifff. fruits was examined by the Shimadzu UV 1800 spectrophotometer. The UV-Vis spectrum of the dye was measured in the range of 200 nm to 800 nm. The dilution of the extracted dye was by 1 mL of dye extract to 50 mL of deionized water.

2.2.4 Experimental design and data analysis

RSM is an effective tool for identifying the optimum set of operational variables for dyeing process development and optimization [28,30,31]. RSM can also identify the interactions, thoroughly covers the design space, and is able to establish the solution with minimal usage of the resources. Traditionally, the optimization of textile dyeing processes has been done by observing the impact of one factor on response output in the absence of changes to other factors (one-factor-at-a-time methodology). However, in textile dyeing processes, the effect of one process variable depends on the others, and the interactions between factors need to be taken into account. In this study, to determine the best combination of experimental dyeing process parameters for optimal color yield of the dyed hemp, RSM was used. Four important dyeing process parameters (dyebath pH, dye concentration, dyeing temperature, and mordant concentration) were assessed using BBD in conjunction with RSM. BBD is a class of second-order response surface design based on three-level incomplete factorial design [22, 28]. BBD are more effective than the three-level full factorial designs because they require fewer runs to generate higher order response surfaces when compared to a normal factorial technique. Preliminary trials were conducted to identify the range of each input parameter and the minimum number of experimental runs, as shown in Table 1. The experimental design, statistical analysis, and optimization of the dyeing process factors were conducted by Minitab software (version 20). According to BBD, a total of 27 experiments were performed. The optimal values of the selected parameters were then determined by solving the regression model equation and analyzing the contour plots of the response surface. In RSM, a polynomial response surface is utilized to illustrate the relationship between a response Y and predicted variables X. The functional relationship for a quadratic model with four experimental variables is presented in Equation (1):

$$\mathrm{Y} = b_0 + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} X_i^2 + \sum_{i=1}^{4} b_{ij} X_i X_j \qquad (1)$$

where Y represents the response function, b_0 is the intercept, b_i, b_{ii} are the coefficients of the quadratic model with four experimental parameters.

To evaluate the significance of each parameter in the predicted model, analysis of variance (ANOVA) was examined and a p-value of less than 0.05 was determined as statistically significant, which means the value indicates statistical significance with a 95% confidence level.

2.2.5 Color measurement and color fastness properties

Each dyed sample was measured for color coordinates and color strength (*K/S*) values on a spectrophotometer (GretagMacbeth LLC, Switzerland). The settings of the apparatus were as follows: illuminant D65, 10° standard observer, and specular and UV included. Each measurement was made three times, and the average values were recorded. The *K/S* values were assessed by using the Kubelka-Munk equation as shown in Equation (2):

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

Where R is the reflectance of the samples at maximum absorption wavelength, *K* is the absorption coefficient, and *S* is the scattering coefficient. For a more accurate comparison of samples across the entire visible spectrum, the sum of color strengths measured at all wavelengths was computed and analyzed further [32].

$$CVsum = \sum_{360}^{740} (K/S) \qquad (3)$$

Table 1. Experimental parameters and range for BBD.

Symbol	Factor	Unit	Lower limit	Upper limit
A	dyebath pH	-	3	9
B	dyeing concentration	%owf	100	200
C	dyeing temperature	°C	60	100
D	mordant concentration	%owf	1	8

The color coordinates of the dyed samples are expressed in terms of the CIELab coordinates (L^*, a^*, b^*), where L^* corresponds to the brightness (100 = white, 0 = black), a^* to the red-green coordinate (+ve = red, -ve = green), and b^* to the yellow-blue coordinate (+ve = yellow, -ve = blue). The C^* value representing chroma (vividness or dullness) and h^o denoting hue angle were calculated using Equation (4) and Equation (5), respectively.

$$C^* = [(a^*)^2 + (b^*)^2]^{1/2} \tag{4}$$

$$h^o = \arctan(b^*/a^*) \tag{5}$$

Color fastness to washing was evaluated following ISO 105-C01. Each dyed fabric (10 cm × 4 cm) was sewed along the four edges with the same size as the multi-fiber fabric. The test samples were then washed in a gyrowash machine at 40°C for 30 min with 5 $g\cdot L^{-1}$ standard soap (ECE), with a liquor ratio of 1:50. After washing, the samples were rinsed in cold water for 10 min. Grayscale was use to evaluate the color change of the test sample and the staining of the adjacent fabric.

Color fastness to water was evaluated following AATCC Test Methods 107. Each dyed fabric (5.7 cm × 5.7 cm) was sewed along the four edges with the same size as the multi-fiber fabric. The test samples were immersed in the DI water for 15 min, and then pressed between the plates of a perspirometer. The test samples, along with the perspirometer, were placed in the oven at 38°C for 18 h, and then graded by grayscale. Grayscale was use to evaluate the color change of the test sample and the staining of the adjacent fabric.

Color fastness to sea water was evaluated following AATCC Test Methods 106. Each dyed fabric (5.7 cm × 5.7 cm) was sewed along the four edges with the same size as the multi-fiber fabric. The artificial sea water medium was prepared by combining 30 g of NaCl, 5 g of $MgCl_2$, and 1 L of distilled water. The test samples were immersed in the sea water medium for 15 min, and then pressed between the plates of a perspirometer. The test samples, along with the perspirometer, were placed in the oven at 38°C for 18 h, and then graded by grayscale. Grayscale was use to evaluate the color change of the test sample and the staining of the adjacent fabric.

Color fastness to perspiration was evaluated following ISO 105-E04. Each dyed fabric (10 cm × 4 cm) was sewed along the four edges with the same size as the multi-fiber fabric. The test samples were immersed in acidic and alkaline mediums for 30 min, and then pressed between the plates of a perspirometer. The test samples, along with the perspirometer, were placed in the oven at 37°C for 4 h, and then graded by grayscale. Grayscale was use to evaluate the color change of the test sample and the staining of the adjacent fabric.

Color fastness to crocking was evaluated following AATCC Test Methods 8. Each test fabric sample (5 cm × 13 cm) was mounted on the bed of the crock meter. Then, a white crocking cloth (5 cm x 5 cm) was mounted on the finger of the crock meter and rubbed against the test fabric sample at a rate of 10 cycles per 10 s. The rubbing effect of the test samples was assessed using grayscale.

Color fastness to crocking was evaluated following AATCC Test Methods 8. Each test fabric sample (5 cm × 13 cm) was mounted on the bed of the crock meter. Then, a white crocking cloth (5 cm × 5 cm) was mounted on the finger of the crock meter and rubbed against the test fabric sample at a rate of 10 cycles per 10 s. The rubbing effect of the test samples was assessed using grayscale.

Color fastness to light was evaluated following ISO 105-B02. The dyed fabrics and blue reference materials, both with the same size of 45 mm by 10 mm, were exposed for 24 h in an Xenon test chamber (Q-sun, USA). Light fastness rating was assessed using the blue scale.

2.2.6 Antibacterial testing

The treated and untreated hemp fabrics were assessed for their antibacterial activity against Gram-positive *S.aureus* (ATCC 6538) and of Gram-negative *E.coli* (ATCC 25922) by both qualitative and quantitative test methods. Qualitative assessment was done by agar diffusion method following AATCC 147 test method. The test samples were cut into circular discs (6 mm in diameter) and sterilized by exposing each side to UV radiation for 30 min. Sterile AATCC bacteriostatic agar was poured in sterile petridishes. 24 h broth cultures of test organisms (*S.aureus* and *E.coli*) were used as inoculums. The test organisms (1×10^5 $CFU\cdot mL^{-1}$) were coated over the surface of the agar plate using a sterile cotton swab and left to dry. The test samples were then carefully placed on the agar plate, on which tetracycline antibiotics were used as positive controls. The agar plates were incubated at 37°C for 24 h. After incubation, the inhibitory action of the tested samples on the growth of the bacteria was observed by measuring the diameter of the clear zone.

The antibacterial activity of the fabric samples was quantitatively evaluated following AATCC Test Method 100 test method. First, the test samples were cut into circular swatches (4.8 cm in diameter) and sterilized by exposing each side to UV radiation for 30 min. Sterile normal saline was employed as a neutralizing solution and a dilution medium. Circular test samples were inoculated with 1.0 mL of inoculums containing either 1×10^5 CFU of *E.coli* or 1×10^5 CFU of *S.aureus*. After incubation at 37°C for 24 h, the percentage reduction (%R) in colony numbers in the treated samples relative to the untreated control was calculated using Equation (6):

$$R\,(\%) = \frac{(B-A)}{B} \text{ x } 100 \tag{6}$$

where R is the percentage reduction in bacterial colonies, A is the number of bacterial colonies from treated sample after inoculation 24 h contact period, and B is the number of bacterial colonies from untreated sample after inoculation at zero contact time.

2.2.7 Evaluation of UV protection

The UV protection property of the pristine and dyed hemp fabrics was evaluated in term of the ultraviolet protection factor (UPF) following the AS/NZS 4399:1996 test method using CamSpec M550 SPF Spectrophotometer (Spectronic CamSpec Ltd, England). The UPF value of each fabric sample was calculated from the total spectral transmittance using Equation (7):

$$UPF = \frac{\sum_{290\,nm}^{400\,nm} E_\lambda S_\lambda \Delta\lambda}{\sum_{290\,nm}^{400\,nm} E_\lambda S_\lambda T_\lambda \Delta\lambda} \tag{7}$$

where Eλ is the relative erythemal spectral effectiveness, Sλ is the solar spectral irradiance, Tλ is the average spectral transmittance of the specimen (measured), and Δλ is the measured wavelength interval (nm).

The average transmittance values in the UV-A and UV-B regions; $T(UV-A)_{AV}$ and $T(UV-B)_{AV}$ are expressed as Equation (8) and Equation (9), respectively.

$$T(UV-A)_{AV} = \frac{\sum_{315\,nm}^{400\,nm} T_\lambda \Delta\lambda}{\sum_{315\,nm}^{400\,nm} \Delta\lambda} \qquad (8)$$

$$T(UV-B)_{AV} = \frac{\sum_{290\,nm}^{315\,nm} T_\lambda \Delta\lambda}{\sum_{290\,nm}^{315\,nm} \Delta\lambda} \qquad (9)$$

3. Results and discussion

3.1 Absorbance of the aqueous extract of *Diospyros mollis Griff.*

An UV absorption spectrum of *Diospyros mollis Griff.* fruits after aqueous extraction is shown in Figure 4. The UV radiation band can be classified into three regions: UV-A band (315 nm to 400 nm), UV-B band (290 nm to 315 nm), and UV-C band (200 nm to 290 nm) [13]. The UV-C band, which is the highest energy region, is totally absorbed by oxygen and ozone in the upper atmosphere. 94% of the solar UV radiation that reaches the earth's surface is in the UV-B spectrum, while only 6% is in the UV-A spectrum. UV-A causes little visible reaction on the skin and decrease the immunological response of skin cell, while UV-B is the most responsible for the development of skin cancer [33]. From Figure 4, it can be observed that the dye extract can absorb radiation in the UV-C, UV-B, and UV-A regions. It can be assumed that absorption in the UV-B area will provide good protection against potentially damaging UV rays.

3.2 Response surface methodology regression

The experimental results of BBD based on four factors with three levels are shown in Table 2. In this study, the considered response or dependent variable was the sum of *K/S* ($CVsum$) whereas the independent variables were the pH of the dye bath, dyeing concentration, dyeing temperature, and mordant concentration. Then, the results were analyzed, and a regression analysis by a quadratic model led to the following equation:

$CVsum$ = -454.6 + 0.67*A + 0.843*B + 10.422*C + 2.37*D - 0.527*A^2 - 0.002*B^2 - 0.059*C^2 - 0.25*D^2 + 0.002*A*B + 0.032*A*C + 0.05*A*D + 0.001*B*C + 0.004*B*D – 0.01*C*D

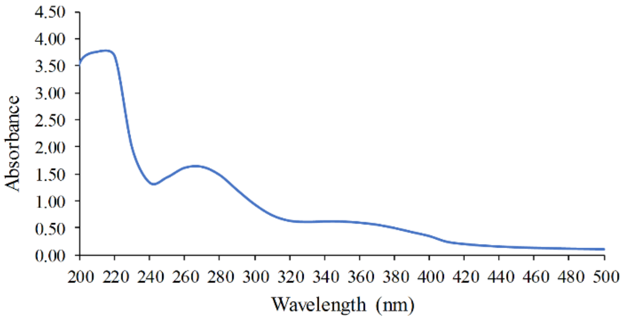

Figure 4. UV spectrum of aqueous *Diospyros mollis Griff.* fruit extract.

where, A is dyebath pH, B is dye concentration, C is dyeing temperature, and D is mordant concentration.

To identify the significant variables and interactions in the dyeing process, the model term having a *p*-value higher than 0.05 is considered as insignificant and eliminated from the final model. The quality of the model fit is expressed by the correlation coefficient (R^2), and its statistical significance is confirmed using the *p*-value. The closer the value of R^2 is to 1, the better the model fit. When the *p*-value for the model is at the 5% level ($p < 0.05$), the regression model is accepted. Otherwise, the *p*-value for lack of fit is higher than 0.05. In this study, the predicted model represents a R^2 of 0.9454, which implies that only 6% of the variation could not be explained by this model. The predicted R^2 demonstrates the accuracy of a regression model in prediction of responses for new trials. The adjusted R^2 is a modified version of the correlation coefficient (R^2) for comparing the ability of models with different number of variables to predict the response. If the difference between adjusted R^2 and predicted R^2 is less than 0.2, the model is sufficiently accurate [24]. In this study, the adjusted R^2 and predicted R^2 are 0.8971 and 0.7712, respectively. In addition, the Fisher's *F*-value (33.92) with a low probability value ($p < 0.05$) suggests that the model was statistically significant, thus the experimental values agree very well with the predicted ones, providing a good predictability of the model. Therefore, it can be concluded that the obtained model has a good predictability within the range of the chosen variables.

The ANOVA results of the applied quadratic model to navigate the design space of hemp fibers dyeing with *Diospyros mollis Griff.* are shown in Table 3. The statistically significant or insignificant factors are determined based on the *p*-values of the independent variables. The *p*-value less than 0.05 suggests that its effect on response is significant. Therefore, it can be inferred that the dyebath pH (A), dyeing conc. (B), dyeing temperature (C), and mordant conc. (D) are the significant factors on the color strength of dyed hemp fiber with *Diospyros mollis Griff.,* due to their low probability values (<0.05) and high F value. Overall, the ANOVA analysis signifies the applicability of the model for the color strength of dyed hemp fabrics with *Diospyros mollis Griff.* extract at the time of the dyeing process within the limits of the experimental factors. A regression analysis of the model equation indicates that the main, square, and the interaction effects of independent variables are significant.

3.3 Effect of dyeing conditions on dyeing quality

In this study, the effects of pH, dyed concentration, dyeing temperature, and mordant concentration on the performance of the dyeing process were investigated. The results were evaluated by measuring the $CVsum$ of the dyed samples. To examine the interaction among the varied independent variables and their corresponding effect on the response, the contour and response surface plots were made as shown in Figure 5. Figure 5(a-b) illustrates the effect of dyebath pH on $CVsum$ values. It is observed that $CVsum$ decreased when the pH of the dye bath was raised from 5 to 9, and the optimum value was obtained at acidic pH 4. The fiber polymer and the dye molecule became more anionic at their hydroxyl sites due to the alkaline pH, creating repulsion between them and thus resulting in lower color strength values [34]. Similar result has been reported in dyeing of hemp fibers with eucalyptus leaf extract which contained similar compounds [35]. Since it modifies the degree of the surface charge and degree of ionization of cellulosic fibers, the pH of a dye bath has a significant impact on the exhaustion of dyes on hemp.

Figure 5(d) presents the effect of dyeing temperature on the $CVsum$ values of the dyed fabrics. As can be seen, it is indicated that the percentage of dye uptake increases with an increase in dye temperature and reaches a maximum value at approximately 90°C. This may be because of the increased kinetic energy of the dye molecules and fiber swelling effects that enhance the dyeing capacity of hemp fibers. Furthermore, the dye solution is comprised of both single molecules and aggregates. Larger aggregates reduce surface adsorption and diffusion rates, which diminish color yield and fastness properties upon surface detachment during washing. Typically, an increase in temperature causes aggregates to disperse and dye exhaustion and color strength to rise, resulting in even and uniform dyeing [34,35]. However, higher dyeing temperatures (above 90°C) decreased the $CVsum$ values, which might be attributed to a decrease in dye molecular stability [34].

Table 2. BBD experimental samples and corresponding response.

Run	Actual level of variable				Response	Color coordinates				
	pH	Dye conc.	Temp.	Mordant conc.	CVsum	*L**	*a**	*b**	*C**	*h*°
1	3	175	80	1.0	91.23	28.95	4.02	5.64	6.93	50.76
2	6	100	60	5.5	85.15	45.21	2.30	1.18	2.59	27.06
3	6	175	80	5.5	84.22	40.61	2.28	2.72	3.55	47.64
4	3	175	100	5.5	30.44	39.26	2.85	5.23	5.96	54.45
5	6	100	100	5.5	35.94	44.26	1.33	0.62	1.47	24.93
6	6	250	80	8.0	95.12	42.38	1.61	3.49	3.84	55.81
7	3	175	60	5.5	100.24	38.51	2.96	4.53	5.41	52.17
8	3	175	80	8.0	97.54	39.54	1.95	2.04	2.79	44.24
9	9	175	100	5.5	93.12	43.89	1.59	1.85	2.44	47.11
10	6	175	80	5.5	51.26	38.90	2.23	1.34	2.6	30.81
11	9	175	80	1.0	100.9	41.63	1.66	1.41	2.18	39.58
12	6	175	80	5.5	85.66	43.77	1.68	2.06	2.66	48.21
13	3	250	80	5.5	44.42	43.84	1.61	1.37	2.11	39.78
14	6	175	60	8.0	91.54	44.73	1.46	1.51	2.15	44.44
15	9	250	80	5.5	96.71	40.82	1.61	2.65	3.17	53.19
16	9	100	80	5.5	84.20	42.97	2.14	4.52	5.37	55.64
17	6	250	60	5.5	85.29	36.62	2.37	5.24	5.71	55.89
18	6	250	100	5.5	73.81	46.81	0.74	2.01	2.14	56.8
19	9	175	60	5.5	40.43	36.17	2.47	3.18	4.03	49.19
20	6	175	100	8.0	92.85	41.85	1.57	0.96	1.84	31.24
21	6	175	100	1.0	79.37	43.23	2.67	1.09	2.88	22.17
22	6	100	80	8.0	91.54	41.73	1.58	1.45	2.14	41.53
23	6	250	80	1.0	90.94	44.75	1.82	0.71	1.95	21.28
24	6	100	80	1.0	87.42	39.58	2.19	3.34	3.99	52.12
25	3	100	80	5.5	98.06	41.25	1.53	0.97	1.81	32.13
26	9	175	80	8.0	53.56	42.80	1.56	0.60	1.67	21.01
27	6	175	60	1.0	101.5	37.34	2.22	4.12	4.68	54.56

Table 3. Regression analysis for the established model.

Source	*F*-value	*P*-value
Model	33.92	0.010
A-pH	27.65	0.020
B-Dye concentration	57.56	0.005
C-Temperature	28.93	0.009
D-Mordant concentration	14.24	0.042
AB	28.05	0.009
AC	36.52	0.040
AD	5.93	0.082
BC	4.28	0.098
BD	16.97	0.025
CD	13.45	0.009
A^2	42.66	0.005
B^2	33.40	0.025
C^2	19.77	0.019
D^2	1.45	0.387

The $CVsum$ of the dyed fabrics increased as the dye concentration was raised from 100%owf to 200 %owf, as shown in Figure 5(a). This is because increasing the concentration of the dye in the solution increases the absorption of dye molecules by the hemp fibers from the dye bath. Typically, the dyeing process engages in adsorption and diffusion [28]. Adsorption is the process by which dyes move from the solution to the surface of the fiber and is affected by various factors, such as the initial concentration of the dye. An increase in the initial dye concentration increases the concentration gradient's driving force, causing a greater amount of dye to be adsorbed onto hemp fibers.

As shown in Figure 5(e-f), the $CVsum$ values of the dyed fabrics with diospyrol extract increase by increasing the concentration of tannic acid mordant. It means that the use of even small amounts of tannic acid caused a significant improvement in the exhaustion of the dye extract and the dye uptake of the mordanted samples. It can be explained that cellulose fiber pre-mordanting with tannic acid provides carboxylic acid groups (-COOH) and additional hydroxyl groups (-OH) in the dyeing system [29,36]. Tannic acid contains hydroxyl groups, unsaturated double bonds, and carboxyl groups, which chemically combine with groups on natural dyes and fibers or form hydrogen bonds and other intermolecular interactions to improve the color strength and color fastness of the dyed cellulosic fabrics. Tannic acid acts as a bridge in dyeing hemp with natural dye, using its –OH groups to make hydrogen bonds with cellulose while –COOH and –OH groups react with natural dye extract. This leads to the formation of a stable compound and fixes the color, as shown in Figure 6.

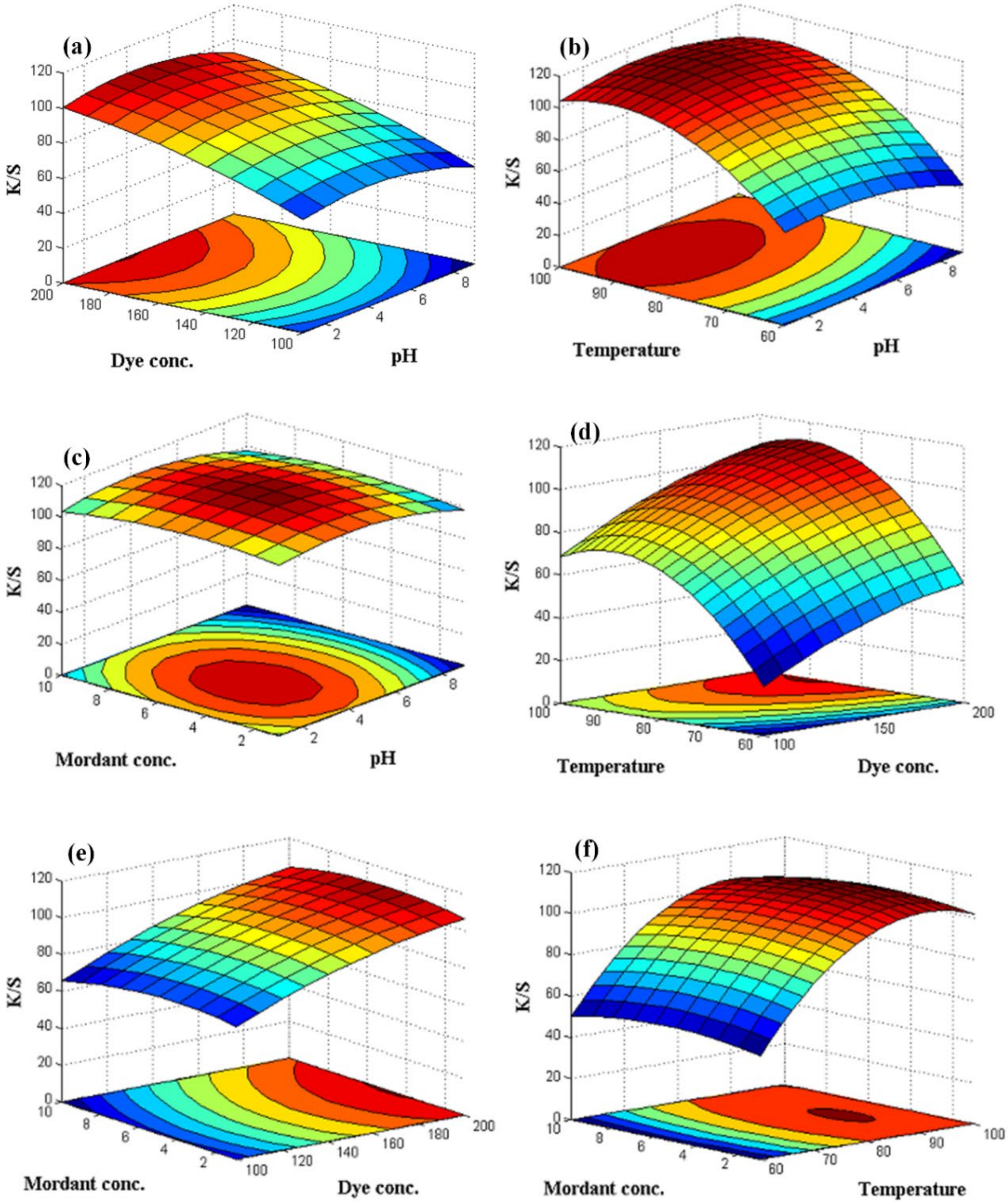

Figure 5. Simultaneous effects of parameters on color strength of dyed hemp fabrics.

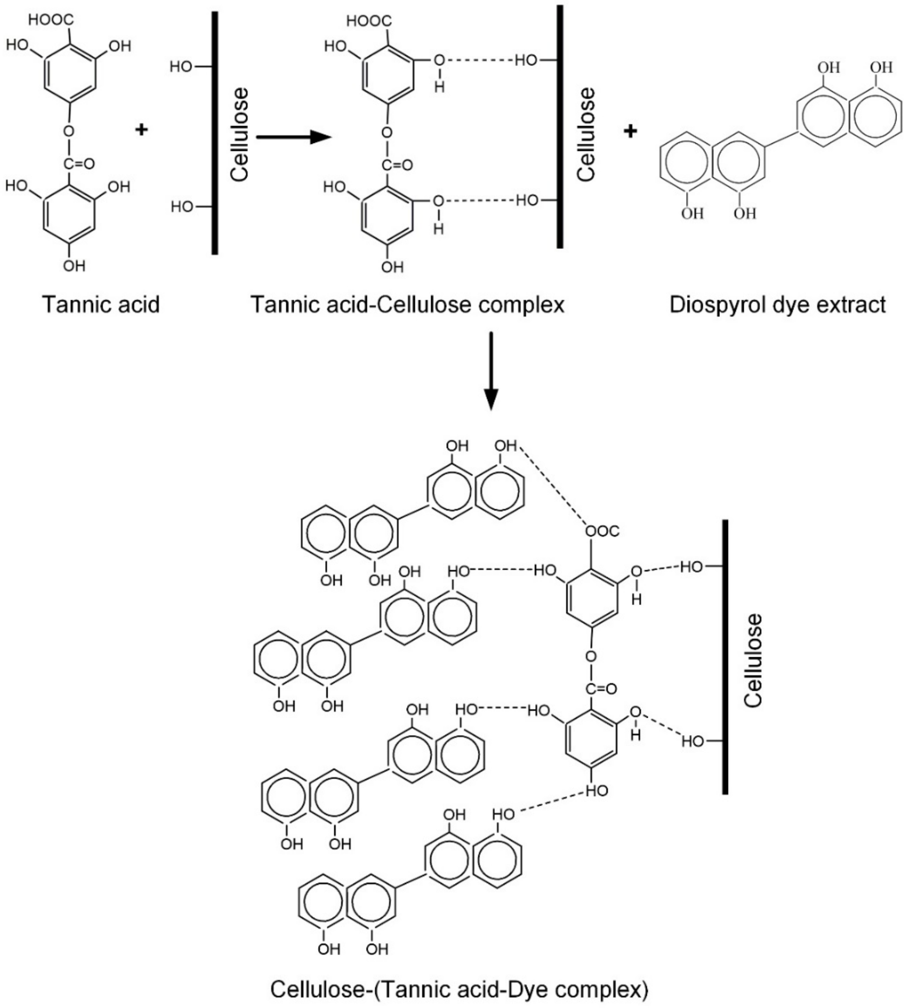

Figure 6. Proposed fixation of diospyrol extract on pre-mordanted hemp.

3.4 Response optimization and validation of the model

The dyeing conditions of hemp fabrics with *Diospyros mollis Griff.* fruit extract were optimized using the optimization function of Minitab. The optimization function examines a combination of factor levels that simultaneously satisfy the goal placed on response and each factor. In this study, the dyeing condition was chosen in the proposed range that obtained the highest value of $CVsum$. Due to that, the proposed optimized conditions for hemp fabric dyeing with berry extract are presented in Table 4. The result obtained when the optimal dyeing conditions are utilized are in accordance with the predicted outcome. Indeed, an experimental $CVsum$ value of 108.24 was obtained vs. a predicted value of 112.65. The model proposed by this study has therefore been validated and confirmed. As a result, the dyeing conditions obtained were used to dye fabric samples for evaluation of color fastness as well as functional properties such as UV protection and antibacterial activity.

3.5 Color fastness testing

Color fastness is the ability of colored textile to retain its original color during normal use, and it is a fundamental requirement for dyed goods marketed commercially. Color fastness is defined by the degree of color change. Table 5-6 present the washing, water, saline solution (simulated sea water), and perspiration color fastness properties of hemp fabrics dyed under the optimal conditions of this study. Most color change values were rated as good to excellent (4-5). The only exception is water exposure, which was rated as fair to good (3-4), indicating that the fixation of diospyrol extract on pre-mordanted hemp fabrics became unstable under these criteria. The polarity of the medium influenced the ionization or dissociation of the phenolic groups of tannic acid-dye complex and hydroxyl groups present in cellulosic hemp fabrics (Figure 6) [2,5]. Color staining, which is defined as the excessive uptake of dye by a substrate due to exposure to a contaminated medium or direct contact with a dyed material, was used to further evaluate the color's stability. To examine this, the dyed samples were wetted with the test medium and placed under constant pressure in direct contact with adjacent multifiber materials. This permits the dye to migrate to the adjacent fabric based on the type of fibers. The degree of color staining on a multifiber fabric composed of acetate, cotton, wool, polyester, acrylic, and nylon, is presented in Table 5. Most degree values of color staining were rated as good to excellent (4-5). The findings indicate that small tannic acid-dye complex molecules migrated from the dyed samples into multifiber fabric. Each fiber type possesses polar end groups such as amino (-NH_2) and hydroxyl (-OH) groups, which may establish hydrogen bond (H-bond) interactions with tannic acid-dye complex molecules that leak off dyed fabrics and contaminate the test media. The color fastness to crocking was also evaluated as shown in Table 6. The color fastness to crocking of the dyed fabrics was rated as good (4) when dry, but rated as poor to fair (2-3) when wet. As predicted, the application of a polar solvent increased the susceptibility of fabrics to color loss upon rubbing, particularly when wet. The light fastness of the dyed fabrics was also good (rated 6). Thus, it is evident that hemp fabrics can be successfully dyed using this natural dye in conjunction with tannic acid as a bio-mordant, resulting in high color yield and good color fastness.

3.6 Antibacterial Activity

Figure 7 shows the antibacterial activity against two key strains of hemp fabrics dyed under the optimal conditions of this study. Their antibacterial activities against *E.coli* (gram-negative) and *S.aureus* (gram-positive) were evaluated following AATCC Test Method 147 [37]. Figure 7(a-b) demonstrates the clear zones of inhibition produced by untreated fabrics, dyed fabrics, and tetracycline antibiotics. Despite the fact that the tetracycline antibiotics had a more potent effect, the dyed fabrics were more effective than the untreated fabrics at inhibiting the growth of microorganisms. Consequently, the quantitative effectiveness of antibacterial activity was measured following AATCC Test Method 100. The untreated fabric (control) and the dyed fabric were compared, and Table 7 summarizes the percentage difference in inhibition as a percentage of reduction. The untreated hemp fabrics exhibited no antibacterial effect against both *E.coli* and *S.aureus*. The antibacterial activity of the dyed fabrics increased significantly. The antibacterial reduction of the dyed fabrics against *E. coli* and *S. aureus* was 97.15% and 92.41%, respectively. Although the dyed fabrics exhibited good antibacterial activity against both *S.aureus* and *E.coli*, it was more pronounced against *E.coli*. The antibacterial activity achieved by the dyed fabric might be because of the presence of tannins and polyphenols in the tannic acid-dye complex. Both polyphenols and hydrolyzed tannin have been shown to have potent antimicrobial properties against human pathogens [32,33].

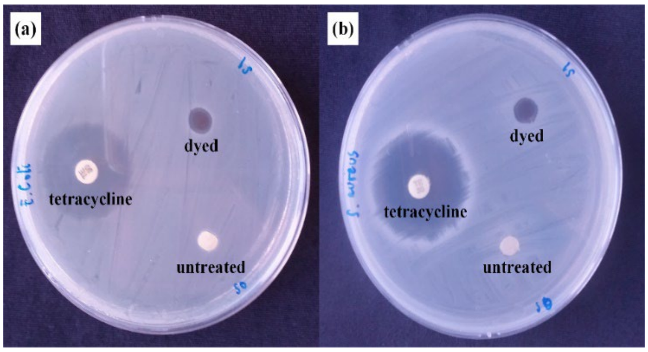

Figure 7. Antibacterial activity against two key strains: (a) *E.coli* and (b) *S. aureus.*

Table 4. Optimal dyeing conditions for obtaining the highest color yield.

A: pH	B: Dye concentration	C:Temperature	D: Mordant concentration	CVsum (predicted)	CVsum (actual)
4	200	92	5.40	112.65	108.24

Table 5. Color fastness properties of dyed fabrics.

Fastness to	Washing	Water	Sea water	Perspiration	
				Acid	Alkaline
Color change	4-5	3-4	4-5	4-5	4
Color staining					
-Acetate	4-5	4	4	4-5	4
-Cotton	4--5	4	4	4-5	4
-Nylon	4-5	4-5	4	4-5	4-5
- Polyester	4-5	4-5	4-5	4-5	5
- Acrylic	4	4	4	4	4
-Wool	4-5	4	4	4-5	4

Table 6. Color fastness to crocking and light.

Color fastness to	Crocking		Light
	Dry	Wet	
Dyed fabric	4	2-3	6

Table 7. UV protection property and antibacterial activity (AATCC 100) of dyed fabrics.

Samples	UPF	UV-A Transmittance (%)	UV-B Transmittance (%)	%Reduction	
				S.aureus	*E.coli*
Untreated	9.82	11.25	7.46	N/A	N/A
Dyed fabric	49.24	2.15	1.99	97.15	92.41

Table 8. The fastness properties and functionalization of black dyes.

Sources	K/S	Washing fastness	Crocking fastness		Light fastness	Antibacterial properties	UPF
			Dry	Wet			
Diospyros mollis Griff./ Hemp (This work)	9.85	4-5	4	2-3	6	%R > 90	49.24
Haematoxylum ampechianum L./ Polyester [41]	3.50	3-4	4-5	3-4	-	Acceptable	-
Leuco sulphur black dye/ Cotton [42]	18.00	4-5	4	2-3	6	-	-

3.7 UV protection

Textiles have been found to offer UV protection property but depending on fiber type, fabric construction, and nature of finishing substances. Color and other UV absorbers on textiles also play a significant role in UV protection [14,36]. Some natural dyes have the ability to absorb in both the UV and visible regions, which allows them to effectively block UV rays while simultaneously coloring [38,39]. To investigate the UV protection property of hemp fabrics dyed under the optimal conditions of this study, UV protection factor (UPF) and UV transmittance parameters are used to determine the protection capacity. UPF is a rating system used for apparels to determine how effectively a fabric shields the skin from UV, whereas percentage transmittance in UV regions determines the penetrability of UV rays to the skin or the effects associated with this. According to the AS/NZS 4399:1996 test method, fabrics with a UPF value in the range 15 to 24 is defined in the standard as offering "good UV protection", from 25 to 39 as offering "very good UV protection", and 40 or greater as offering "excellent UV protection". In addition, the UV protection property of the dyed fabric is evaluated as “good” when the UV transmittance is less than 5%. For this study, UPF values and percent transmittance of UV-A (315 nm to 400 nm) and UV-B (290 nm to 315 nm) radiations of pristine and dyed hemp fabrics were detected and shown in Table 7. The results show a significant difference between the pristine and dyed fabrics. The pristine hemp fabrics used in this study had a low UPF of 9.82. Therefore, unless specially treated, pristine hemp fabrics do not provide sufficient skin protection against UV radiation. As the dyed hemp fabric contains polyphenolic compounds that can absorb UV radiation [35,36], it offers superior UV protection compared to untreated fabric, as evidenced by the higher UPF values and lower UV transmittance percentage (Table 7). The UPF of the dyed fabrics also achieved the maximum (40+) level, highlighting the excellent UV shielding property of the dyed hemp fabrics. This is expected because, in general, fabrics treated with dark-colored dyes exhibit a higher UPF, particularly at high dyeing concentrations.

The dyeing and functionalization of hemp fabrics using the extract showed a black color and an acceptable range of fastness properties, antibacterial properties, and UV resistance. One other important black natural dye is Logwood (*Haematoxylum campechianum*), which is also known as Campeachy wood [40]. It had been used for dyeing silk in deep shades on an iron tannate mordant. Table 8 summarizes the recent studies of black dyes and their functionalization; the results are comparable to ours.

4. Conclusion

This study has investigated the potentially of *Diospyros mollis Griff.* to be used as a natural dye and a multifunctional finishing agent for cellulosic hemp fabrics. The *Diospyros mollis Griff.* colorant was successfully extracted and utilized in dyeing of hemp fabrics using tannic acid as a bio-mordant through an eco-friendly and economical method. The natural dyeing processes were optimized by RSM for the highest color yield. The optimal conditions were determined and confirmed to be pH 4, dyeing concentration of 200 %owf, dyeing temperature of 92°C, and mordant concentration of 5.4 %owf. To validate the optimal conditions, performance evaluations were conducted, including color fastness properties of the dyed hemp fabrics as well as functional properties like antibacterial activity and UV-protection. The resulting fabrics had a black hue, and were rated as good to excellent (ratings > 4) for color fastness against washing, water, sea water, and perspiration. The light fastness of the dyed fabrics was also good (rated 6). The dye fabrics showed a good antibacterial activity (bacterial colony reduction > 90%) against *E.coli* and *S.aureus*, however it was more pronounced against *E.coli*. The UPF of the dyed fabrics also achieved the maximum (40+) level, highlighting the excellent UV shielding property of the dyed hemp fabrics. Thus, aqueous extracts of *Diospyros mollis Griff.* fruits can be utilized as a natural black dye and anti-UV and antibacterial finishing agents for textile substrates to produce value-added eco-friendly products.

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