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Bioactive and Multifunctional Wool Textiles Finishing with *Diospyros mollis Griff.* Extract

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Abstract

Due to the sudden pandemic outbreak, there is a substantial demand for antimicrobial textiles for health and hygiene. Natural dyeing with plant sources has been proven to be an excellent eco-friendly method for producing healthcare textiles. In this study, *Diospyros mollis Griff.* extract was applied to the simultaneous dyeing and multi-functionalization (antibacterial activity and UV-protection) of wool fabrics. Response surface methodology was applied to optimize the treatment procedure and assess parameter interactions. The optimal result was achieved when dyeing at pH 4, dye concentration 25 g/L, temperature 88°C, and time 95 min. The dyed fabrics had good antibacterial activity against both *E.coli* and *S.aureus* (bacterial colony reduction > 90%), with *E.coli* being more pronounced. The UV protection factor (UPF) also reached the maximum (40+) level, demonstrating their superior UV protection. The finished wools are black, with high color strength (K/S > 9), good light and washing fastness, and fair to good crocking fastness. Thus, *Diospyros mollis Griff.* fruit extract can be used as a new bioactive agent for multifunctional textiles, as well as simultaneous black coloring.

***Keywords*:** *Diospyros mollis Griff*; Wool; Functional textile; Antibacterial activity; UV-protection; Response surface methodology

1. Introduction

As a result of the sudden outburst of COVID-19 pandemic, there is a huge market for antimicrobial textiles for health and hygiene (Saber, & EI-Aziz, 2022). In addition to medical and healthcare products, potential markets include clothes and apparel, home textiles, and worker uniforms. Wool dominates the natural textile business because of its diverse properties, which include natural softness, dyeability in a variety of colors, good heat insulation, wrinkle resistance, and fire resistance (Allafi et al., 2022; Shabbir et al., 2020). Unfortunately, wool fiber is prone to microbial growth and multiplication. It provides an ideal environment (protein nature and moisture absorption) for the growth and propagation of pathogenic microorganisms when in contact with the human body, leading to skin diseases, odors, irritations, infections, and other related symptoms (Shabbir et al., 2020). Transmission via contaminated surfaces has been recognized as a significant route for spreading the pathogen (Chitichotpanya et al., 2022). To prevent contamination, inhibit microbial growth, and enhance the functionality of wool simultaneously, treatment with functional natural dyes is an eco-friendly approach (Benkhaya et al., 2020; Yadav et al., 2023).

Natural dyes are typically extracted with water from their natural color sources (plants, microorganisms, animals, and minerals) (Nambela et al., 2020). These dyes can be used for coloration of textile fibers, as well as other substrates such as hair, skin, paper, candle, and food. Some natural dyes contain bioactive phytoconstituents that impart functionalities to substrates such as insect repellent, deodorizing, antioxidant, antimicrobial, and UV-protective properties, besides their distinctive colors and tones (Chakraborty et al., 2020; Yemiş et al., 2022; Inprasit et al., 2018; Shabbir et al., 2018; Grifoni et al, 2020). Based on their chemical structure, natural dyes can be categorized as carotenoids, quinoids, flavonoids, indigoids, tannins, pyridine-based, and dihydropyrans (Mansour, 2018). The most prevalent natural dyes are the carotenoids, quinoids, flavonoids. Of these, the carotenoids and flavonoids have received the most attention. Polyphenolic compounds, flavonoids, flavones, and tannins from plant dyes have been shown to absorb visible light and UVB, thereby reducing their transmission through substrates (Grifoni et al., 2020; Vuthiganond et al., 2020). Additionally, natural dyes containing polyphenols and phenolic compounds can be considered as broad-spectrum antibacterial agents (Baseri, 2022; Inprasit et al., 2018; Inprasit et al., 2020). In recent years, numerous efforts have been devoted to identifying new sources of natural dyes, reintroduce traditional natural dyes into modern dyeing practices, optimize process conditions for their application, modify application methods, and enhance dyeing efficiency (Nambela et al., 2020; Shahid & Mohammad, 2013; Haji, & Naebe, 2020).

Diospyros mollis Griff., known as 'Makleua' in Thai, has been used as a medicinal plant for centuries. It belongs to the family Ebenaceae and is predominantly cultivated in Southeast Asian countries. Its fruit extract contains a readily oxidizable phenolic compound known as diospyrol ($C_{22}H_{18}O_4$), or tetrahydroxyl dimethyl bi-naphthalene (Yoshihira et al., 1971; Suwama et al., 2018), which has been used as an anthelmintic and a traditional black dye for silks. Diospyrol is susceptible to air oxidation, and consequently, it turns black when exposed to air. The formation of the black colorant is involved polymerization due to phenol radical coupling, quinone-phenol rearrangement, and the formation of a phenol-quinone charge-transfer complex, as demonstrated in Figure 1 (Yoshihira et al., 1971; Wang et al., 2018). Thus, *Diospyros mollis Griff* is a source of bioactive compounds that can be used as a natural black quinone dye. Previous research shows that natural quinone dye compounds are abundant, albeit in modest quantities, but all have the potential for increased production. In addition, they exhibit superior dyeability, stability, brightness, and fastness in comparison to alternative natural dyes like carotenoids and anthocyanins (Dulo et al., 2021). However, it has received little attention as a source of plant dye to color or functionalize textile materials. According to our review of the scientific literature, few studies have been conducted on the use of *Diospyros mollis Griff.* extract in textile dyeing. (Thi et al., 2016; Phuong, 2020). In addition, no studies have been conducted on the fruit extract of *Diospyros mollis Griff.* as a functionalization agent for antibacterial activity and/or UV protection in wool textiles.

The expanding market for medical and healthcare textiles has created numerous opportunities for the use of natural colorants to impart functional finishes. The use of natural dyes to impart UV protection or antibacterial activity has been reported in literature (Chakraborty et al., 2020; Yemiş et al., 2022; Inprasit et al., 2018, Inprasit et al., 2020; Pisitsak et al., 2018; Sadeghi-Kiakhani et al., 2021; Agnhage et al., 2017; Vuthiganond et al., 2020). This study aims to promote the use of Diospyros mollis Griff., a provincial tree in Suphanburi Province, in functional textile dyeing through a scientific approach. In the present study, we hypothesized that *Diospyros mollis Griff.* fruit extract would act as a source of bioactive dye for coloration, antibacterial activity, and UV protection on wool fibers due to the chemical composition of diospyrol. To achieve the desired results, natural dyeing requires a delicate balance of treatment conditions and application techniques (Alebeid et al., 2020). Optimization of process variables is one of the crucial techniques for advancing the natural dyeing process. Hence, the response surface methodology (RSM) in conjunction with Box-Behnken design (BBD) was used to investigate the significant effects of dyeing process factors (pH, dye concentration, temperature, and time) on color strength of dyed wool fabrics. RSM has proven to be a useful method for determining an appropriate set of operational factors for optimizing the dyeing process (Shahid et al., 2017; Sinha et al., 2016; Haji, 2020; Yu et al., 2019; Haji, & Rahimi, 2020).

Furthermore, it can identify interactions, exhaustively cover the design space, and requires fewer experimental trials than the classic one-factor-at-a-time method. To validate in practice the optimal conditions determined by RSM, performance assessments, such as color characteristics, color fastness, antibacterial activity, and UV protection, were performed in accordance with AATCC, ISO, and AS/NZS Test Method standards.

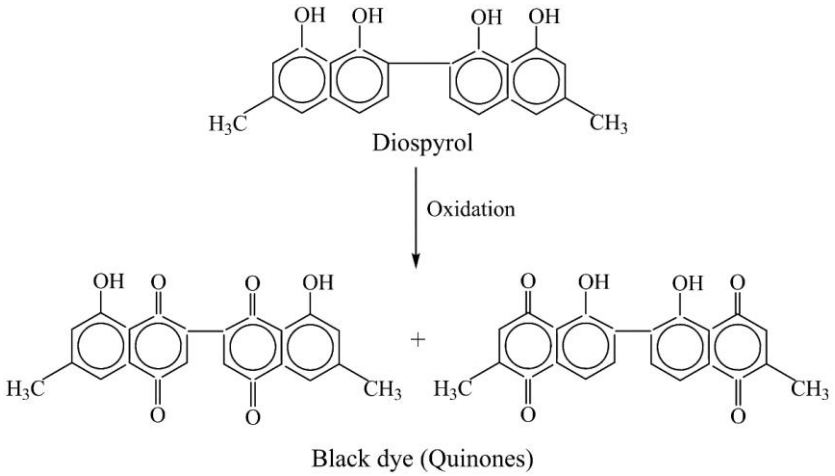

Figure 1 The formation of black quinone colorant

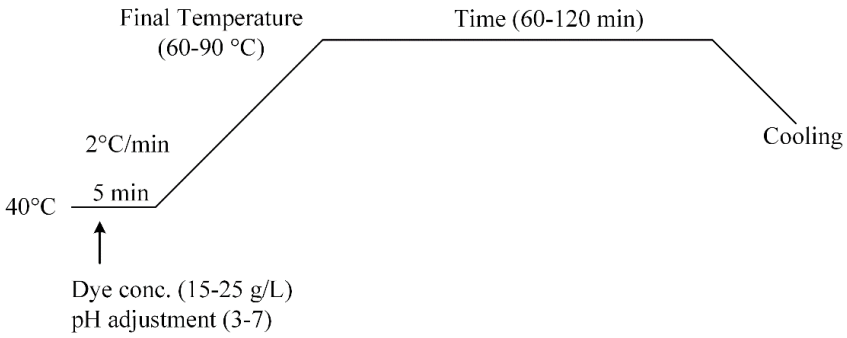

Figure 2 Schematic diagram of dyeing procedure

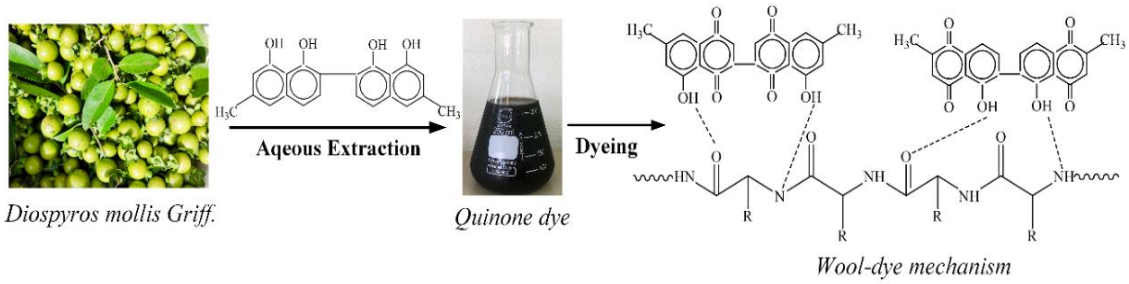

Figure 3 Dyeing mechanism.

2. Materials and methods

2.1 Materials

A 100% pure wool fabric with fabric thickness of 0.35 and mass per unit area of 147 g/m^2 was used in this study. The fabric was scoured for 30 min at 50°C with 4 g/L nonionic detergent to remove contaminants, then rinsed and air-dried at room temperature. Dried fruits of *Diospyros mollis Griff* were obtained from Suphanburi Province, Thailand. The pH was adjusted using sodium hydroxide (NaOH) or hydrochloric acid (HCl) of analytical grade purchased from Sigma-Aldrich (Thailand) Company Limited.

2.2 Methods

2.2.1 Dye extraction

The fruits of Diospyros mollis Griff were washed thoroughly and sun-dried until a constant weight was obtained. They were then pulverized and extracted for an hour in an infrared dyeing apparatus (Starlet DL-6000, Korea) using boiling water (1:10 w/v). The dye solution was obtained by filtering the mixture through Whatman No. 1. Finally, the concentration of the dye solution was adjusted to 10 wt%, and its pH was 3.95.

2.2.2 Dyeing procedure

Aqueous extract of *Diospyros mollis Griff.* fruits were used for dyeing wool fabrics and keeping a material to liquor ratio of 1:30. All of the dyeing processes were carried out in an infrared dyeing machine (Starlet DL-6000, Korea) using an exhaust method, as shown in Figure 2. The pH was adjusted via the addition of 1 M solution of HCl or NaOH. After that, the dyed fabrics were washed at 50°C for 30 minutes with 2 g/L of the 1993 AATCC Standard Reference Detergent without optical brightener to get rid of excessive and unfixed dyes. The samples were then washed with water and dried at room temperature. These result in the formation of a stable dye that fixes the color on wool fabrics, as shown in Figure 3.

2.2.3 UV-vis spectroscopy analysis

The absorption spectra of the aqueous dye extracted from the *Diospyros mollis Griff* fruits were collected using a Shimadzu UV 1800 spectrophotometer. The absorption spectrum of the extracted dye was measured between 200 and 800 nm. The dye's UV-vis spectrum was measured between 200 and 800 nanometers. The extracted dye with a 10 wt% concentration was diluted by mixing 1 mL of dye solution with 40 mL of deionized water.

2.2.4 Experimental design and data analysis

The design of experiment, data analysis, and dyeing process optimization were implemented using Minitab software. The RSM was used in conjunction with BBD to examine the four effects of the dyeing process on the *K/S* values of the dyed wools: pH, dye concentration, temperature, and time. BBD is a class of second-order response surface design based on three-level incomplete factorial design (Box, & Wilson, 1951). Preliminary tests were conducted to determine the appropriate input parameter range for the dyeing process, as stated in Table 1. A total of 27 experiments were carried out according to BBD (Table 2). The quadratic regression model with four experimental variables is represented in Equation (1):

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

where Y is the response or dependent variable, b_0 is the intercept, and b_i, b_{ii} are the quadratic model coefficients.

An ANOVA (analysis of variance) was performed to evaluate the significance of the model's main effects and interactions between factors. A *p*-value less than 0.05 was considered to be statistically significant with a 95% level of confidence.

Table 1 Experimental design levels for BBD

Symbol	Independent Variables	Unit	Lower bound	Upper bound
A	pH	-	3	7
B	dye concentration	g/L	15	25
C	dyeing temperature	°C	60	90
D	dyeing time	min	60	120

2.2.5 Color measurement and fastness properties

The color coordinates and color strength (*K/S*) values of the dyed wool fabrics were measured with a spectrophotometer (GretagMac beth LLC, Switzerland) with illuminant D65, 10° standard observer, and specular included. Each measurement was done three times, and the mean values were complied. Using the Kubelka-Munk equation, as shown in Equation (2), the *K/S* values were calculated:

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

where *K* represents the absorption coefficient, *S* the scattering coefficient, and R the reflectance at maximum absorption wavelength.

The color coordinates are expressed using CIELab color space (*L**, *a**, *b**), with *L** corresponding to brightness (100 = white, 0 = black), *a** to red-green coordinate (+ve = red, -ve = green), and *b** to yellow-blue coordinate (+ve = yellow, -ve = blue). *C** value corresponding to chroma and h^o value to hue angle are computed using Equation (3) and Equation (4), respectively.

$$C^* = [(a^*)^2 + (b^*)^2]^{1/2} \quad (3)$$

$$h^o = \arctan(b^*/a^*) \quad (4)$$

Color fastness to light, crocking, and washing were assessed following ISO 105-B02:1994, AATCC Test Methods 8-2013, and AATCC Test Methods 61-2013, respectively.

2.2.6 Evaluation of UV protection

The UV protection property of untreated and dyed fabrics was quantified via the measurement of the Ultraviolet Protection Factor (UPF) using a CamSpec Spectrophotometer (Spectronic CamSpec Ltd, England) in accordance with AS/NZS 4399:1996. The UPF value was calculated from the total spectral transmittance using Equation (5):

$$UPF = \frac{\Sigma_{290\ nm}^{400\ nm} E_\lambda S_\lambda \Delta\lambda}{\Sigma_{290\ nm}^{400\ nm} E_\lambda S_\lambda T_\lambda \Delta\lambda} \quad (5)$$

where S_λ is the solar spectral irradiance, E_λ is the relative erythemal spectral effectiveness, T_λ is the measured average spectral transmittance of the specimen and $\Delta\lambda$ is the measured wavelength interval (nm).

The average transmittance values in the UV-A and UV-B zones are represented by Equation (6) and Equation (7), respectively.

$$T(UV\text{-}A)_{AV} = \frac{\Sigma_{315\ nm}^{400\ nm} T_\lambda \Delta\lambda}{\Sigma_{315\ nm}^{400\ nm} \Delta\lambda} \quad (6)$$

$$T(UV\text{-}B)_{AV} = \frac{\Sigma_{290\ nm}^{315\ nm} T_\lambda \Delta\lambda}{\Sigma_{290\ nm}^{315\ nm} \Delta\lambda} \quad (7)$$

2.2.7 Antibacterial activity testing

The treated and untreated wool 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 conducted by an agar diffusion method following AATCC Test Method 147. The test samples were cut into 6-mm-diameter discs and sterilized by exposing each side to 30 min of UV radiation. 24 h broth cultures of test organisms (*S.aureus* and *E.coli*) were used as inoculums. The test organisms (1 x 10^5 CFU/ml) were dispersed throughout the surface of the agar plate and allowed to dry. The test sample was then meticulously put on the agar plate alongside the tetracycline antibiotics that served as the positive control. The agar plates were incubated for 24 hours at 37 °C. After incubation, the inhibitory effectiveness of the tested samples on the growth of the bacteria was determined by measuring the diameter of the clear zone.

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

$$R\ (\%) = (B-A)/B \times 100 \quad (6)$$

where R is the percentage reduction in bacterial colonies, A is the number of bacterial colonies from treated fabric swatch after 24 hours of incubation, and B is the number of bacterial colonies from the untreated sample before incubation.

3. Results and Discussion

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

Figure 4 displays an UV absorption spectrum from 200 to 500 nm of aqueous *Diospyros mollis Griff.* fruit extract. The UV radiation mainly include UV-A band (315-400 nm), UV-B band (290-315 nm), and UV-C band (200-290 nm). In the upper atmosphere, oxygen and ozone absorb the high-energy UV-C spectrum. Approximately 95% of the solar UV radiation that reaches the earth surface is UV-B, whereas only 5% is UV-A (Rivas et al., 2020). UV-A causes little visible skin reaction and reduces the immune response of skin cells, whereas UV-B is the primary cause of skin cancer development (Mongkholrattanasit et al., 2014). From Figure 4, it can be seen that the extract can absorb radiation in the UV-C, UV-B, and UV-A regions. It can be suggested that absorption in the UV-B area could offer sufficient protection against harmful UV rays.

3.2 Regression analysis

Table 2 presents the experimental outcomes of BBD with three levels and four variables. The *K/S* is the response or dependent variable, while the independent variables were the dyebath pH, dye concentration, temperature, and time. The data was then analyzed, and a quadratic regression model produced the following equation. The considered response or dependent variable was the *K/S*, while the independent variables were the pH of the dye bath, dye concentration, dyeing temperature, and dyeing time. Then, the results were analyzed, and a quadratic regression model yielded the following equation:

$$K/S = -5.79 + 1.418*A + 0.279*B + 0.051*C + 0.114*D - 0.27*A^2 - 0.009*B^2 - 0.001*C^2 - 0.001*D^2 + 0.007*A*B + 0.004*A*C + 0.003*A*D + 0.003*B*C$$

where A denotes the dyebath pH, B the dye concentration, C the temperature, and D the time.

An ANOVA (Table 3) was used to determine the statistical significance of the BBD model. Model terms with *p*-values larger than 0.05 are considered insignificant and are removed from the final model. The correlation coefficient (R^2) measures the quality of the model fit, and the *p*-value confirms its statistical significance. The closer R^2 gets to 1, the better the model fits. If the *p*-value of the regression model is less than 5% ($p < 0.05$), it is accepted. If this is not the case, the *p*-value for lack of fit is more than 0.05. In this investigation, the predicted model had an R^2 of 0.9554, indicating that it could only explain 4% of the variation. The anticipated R^2 represents a regression model's predicting accuracy for new trials. The adjusted R^2 is a modified form of the R^2 used to examine the predictive power of models with different number of variables. The model is considered accurate if the difference between adjusted R^2 and predicted R^2 is less than 0.2 (Shahid et al., 2017). The adjusted R^2 and predicted R^2 values in this study are 0.8782 and 0.7824, respectively. Furthermore, the F-value of the model (148.35) with a low probability value ($p < 0.05$) suggests that the model was statistically significant; consequently, the experimental values agree well with the projected values, confirming the model's good predictability. It is possible to conclude that the produced model has a good level of predictability within the given variable range.

Table 4 shows the linear coefficients (A, B, C, and D), quadratic coefficients (A^2, B^2, C^2, and D^2), and interaction coefficients (AD and BC) are significant with $p < 0.05$. The coefficients of the other terms are not significant ($p > 0.05$). As a result, A, B, C, D, A^2, B^2, C^2, D^2, AD, and BC play important roles in defining the K/S values of dyed wool materials. Within the boundaries of the experimental variables, the ANOVA analysis reveals that the model equation for the color strength of dyed wool fabrics using *Diospyros mollis Griff.* fruit extract during the dyeing process is applicable. The main, square, and interaction effects of independent variables are all significant, according to a regression analysis of the model equation.

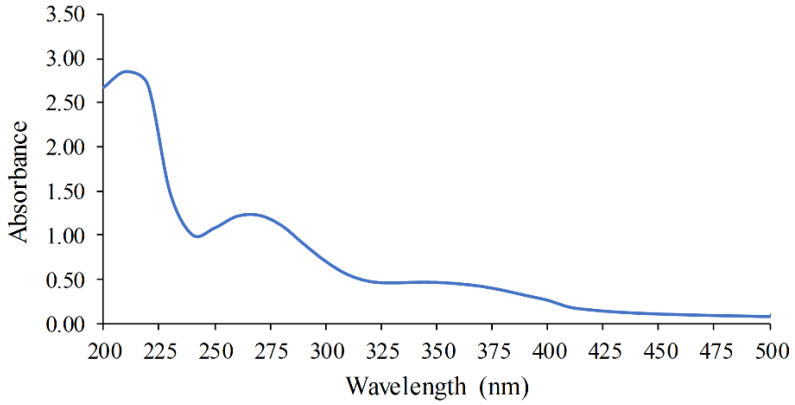

Figure 4 UV spectrum of aqueous *Diospyros mollis Griff.* fruit extract

Table 2 BBD experimental samples and corresponding response

Run	Independent variables				Response	Color values				
	pH	Dye conc.	Temp	Time	*K/S*	*L**	*a**	*b**	*C**	*h°*
1	7	20	60	90	4.94	45.87	3.28	0.57	3.33	9.86
2	3	20	75	120	8.35	28.88	3.13	2.34	3.91	36.31
3	5	15	60	90	7.31	31.75	2.95	2.02	3.58	34.07
4	5	25	75	60	8.56	27.14	1.66	1.12	2.00	33.69
5	5	20	90	60	7.81	28.97	3.89	1.18	4.07	16.87
6	5	20	75	90	8.64	25.72	3.58	1.24	3.79	19.09
7	3	25	75	90	9.41	26.87	2.17	2.19	3.08	43.86
8	5	25	75	120	7.88	29.65	2.62	0.87	2.76	18.36
9	3	20	90	90	8.21	26.33	2.07	1.54	2.58	36.18
10	7	15	75	90	5.22	44.43	3.11	3.01	4.33	42.84
11	7	20	90	90	6.45	38.63	1.44	2.42	2.82	53.45
12	5	25	60	90	8.71	26.04	1.99	1.17	2.31	30.28
13	5	20	60	120	7.79	30.56	1.55	0.24	1.57	8.80
14	5	20	60	60	6.54	37.58	3.21	2.81	4.27	40.34
15	7	25	75	90	5.24	43.61	2.15	2.88	3.59	49.94
16	3	20	75	60	8.11	29.11	2.24	1.75	2.84	37.44
17	5	15	75	60	6.71	35.14	0.99	2.59	2.77	56.69
18	5	15	75	120	4.98	46.22	1.85	1.72	2.53	41.85
19	5	15	90	90	7.26	32.45	3.05	1.89	3.59	31.56
20	3	15	75	90	7.68	29.99	2.61	1.57	3.05	30.83
21	5	20	75	90	8.64	26.94	2.11	2.56	3.32	47.99
22	3	20	60	90	8.54	27.99	3.12	0.87	3.24	15.57
23	5	25	90	90	9.36	27.22	3.54	1.85	3.99	27.48
24	7	20	75	120	6.19	37.79	2.51	2.64	3.64	44.83
25	7	20	75	60	5.04	45.74	1.77	2.55	3.10	51.21
26	5	20	75	90	7.22	31.84	2.47	0.99	2.66	21.81
27	5	20	90	120	8.74	27.37	3.49	0.99	3.63	15.83

Table 3 ANOVA analysis of experimental data fitted quadratic model.

Source	DF	Sum of Square	Mean Square	F-value	P-value
Model	14	37.256	2.661	148.35	0.000
Linear	4	29.732	7.433	314.37	0.000
Square	4	7.129	1.782	99.35	0.000
Interaction	6	0.395	0.066	3.66	0.026
Residual	12	1.215	0.057		
Lack of fit	10	1.215	0.065	17.72	0.001
Pure error	2	0.002	0.002		
Total	26	37.471			

Table 4 Regression analysis for the fitted quadratic model.

Source	Coefficient estimate	Standard error	*F*-value	*P*-value
A-pH	-1.238	0.039	425.17	0.000
B-Dye conc.	0.923	0.039	270.33	0.000
C-Temperature	0.147	0.039	14.39	0.003
D-Time	0.266	0.039	47.60	0.000
AB	0.068	0.065	1.02	0.333
AC	0.110	0.065	2.70	0.126
AD	0.177	0.065	7.01	0.021
BC	0.225	0.065	11.29	0.006
BD	-0.012	0.065	0.03	0.855
CD	-0.001	0.065	0.00	1.00
A^2	-1.085	0.058	250.02	0.000
B^2	-0.216	0.058	13.86	0.003
C^2	-0.178	0.058	33.86	0.010
D^2	-0.592	0.058	104.20	0.000

3.3 Effect of dyeing conditions on color strength

The effects of pH, dye concentration, temperature, and time on color strength of the dyeing process were investigated. The contour and response surface plots shown in Figure 6 were created to analyze the interaction between the various independent variables and their corresponding effect on the response. As shown in Figure 6 (a, b, and c), the *K/S* values of dyed wool fabrics decreased as the pH of the dye solution increased. Observations indicate that the optimal values are obtained at pH 4. Changes in the chemical structure of dye molecules and wool fibers at different pH values have a significant impact on the adsorption of dyes on wool surface. Dye molecules composed of hydroxyl groups (-OH) attain more negative charges as the pH increases. Wool fiber would gain more negative charges when increasing the pH due to the ionization of carboxylic acid groups (-COOH) in wool structure (Figure 5). Thus, increasing the dyebath pH increased the repulsive forces between the dye molecules and the wool fibers, resulting in decreased dye absorption and *K/S* value in the dyed fabrics at higher pH values. Haji et al. demonstrated that an increase in pH neutralizes the positive charge of amino groups in wool, resulting in reduced electrostatic interactions and consequently decreased dye adsorption on wool fibers (Haji, & Rahimi, 2020).

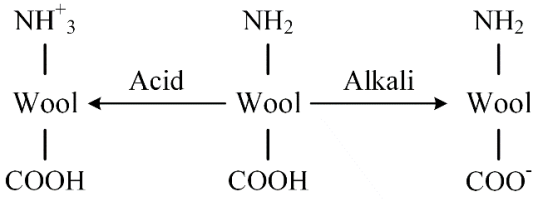

Figure 5 Effect of different pH values on wool ionization

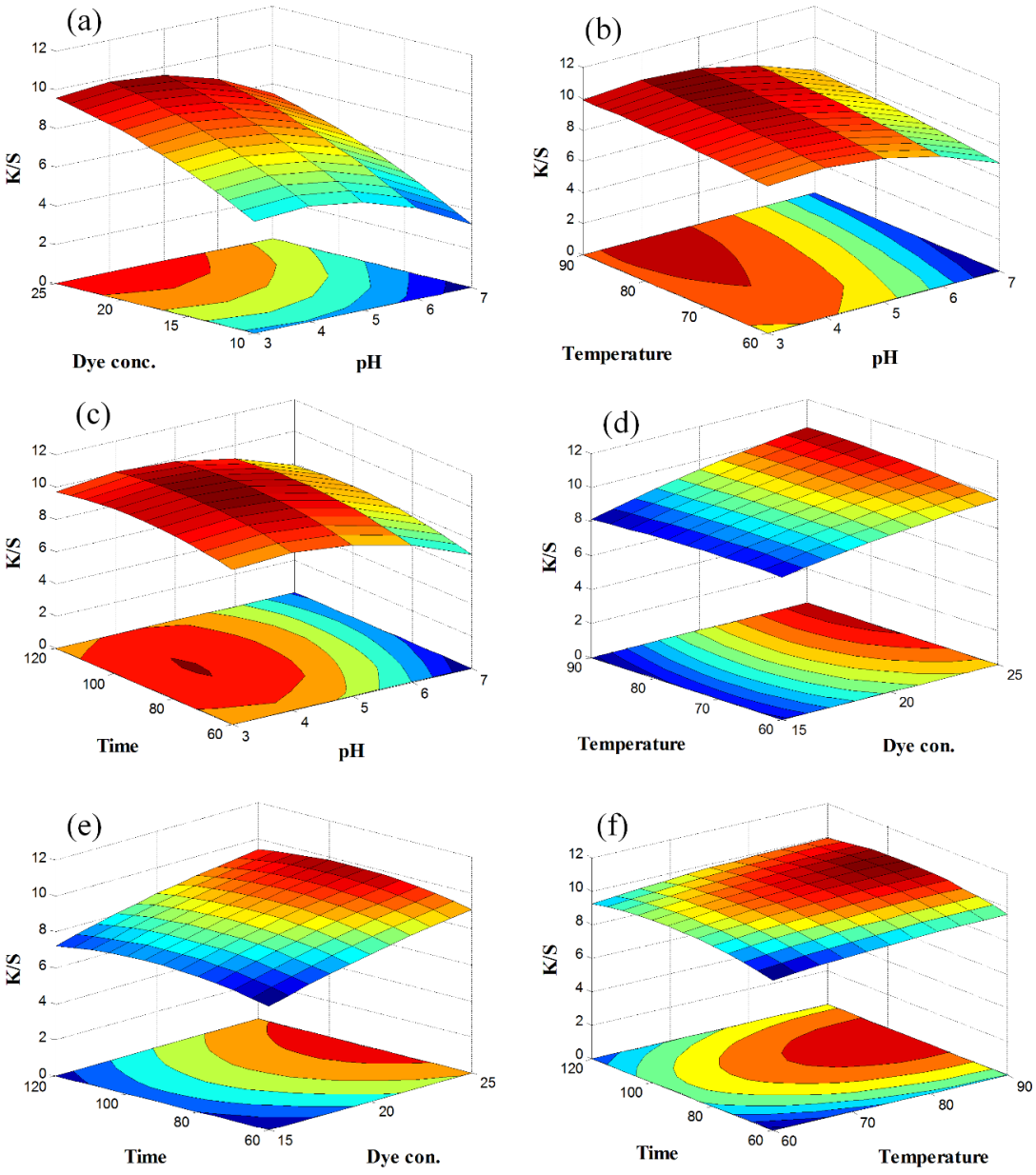

Figure 6 Interaction effects of factors on color strength of the dyed wool

Both pH and temperature play important roles in natural dyeing processes and are regarded as the most influential factors on dye binding to fiber surface (Shahid et al., 2017). The response surface plot (Figure 6 (b)) indicates a relationship between the pH and temperature of the dye solution in order to achieve the greatest color depth. At all temperatures, increasing the pH resulted in a decrease in K/S values.

Figure 6 (a, d, and e) represent the interactive effect of dye concentration on pH, time, and temperature. The color strength gradually increased as the dye concentration increased from 15 to 25 g/L. This is because increasing the concentration of the dye in the solution enhances the absorption of dye molecules by the wool fibers. However, in a high dye concentration range, the increase in color strength with increasing dye concentration was substantially reduced, possibly due to the decreased dyeing sites of wool fibers. This is a common phenomenon in dyeing processes. The effect of dyeing temperature and time on *K/S* values was more noticeable at higher dye concentrations.

Figure 6 (b, d, and f) represent the interactive effect of dyeing temperature on pH, dye concentration, and time. They show that the percentage of dye uptake increases with dye temperature and reaches a maximum at around 89 ℃. This could be due to the higher kinetic energy of the dye molecules and the fiber swelling effect, both of which enhance the dyeing capacity of the wool fibers. Furthermore, the dye solution contains single molecules as well as aggregates. Larger aggregates reduce diffusion rates and surface adsorption, lowering color strength and fastness. Increased temperature typically allows aggregates to disperse while also increasing dye exhaustion and color strength, resulting in complete and uniform dying (Baig et al., 2020). Higher dyeing temperatures (above 89°C) reduce *K/S* values because the desorption rate of dye molecules may become greater than adsorption at such temperatures (Shahid et al., 2017).

Figure 6 (c, e, and f) represent the interactive effect of dyeing time on pH, dye concentration, and temperature. As can be seen, the dye uptake by wool fibers was depended on time. Color strength increased at initially, then fell, with the highest *K/S* value occurring in the middle of the dyeing process. This could be because the dye molecules were rapidly adsorbed at first due to the abundance of dyeing sites, but as the amount of dye fixed to the fiber reaches the saturation mode, the desorption rate increases, leading to decreased *K/S* values.

3.4 Response Optimization and validation of the model

Minitab's optimization function was utilized to optimize the conditions for dyeing wool fabrics with *Diospyros mollis Griff.* fruit extract. The optimization function examines a set of factor levels that achieve the goal placed on response or dependent variable. In this study, the dyeing condition with the highest K/S value was selected from the provided range. As a result, Table 5 shows the proposed optimum conditions for wool fabric dyeing with natural dye extract. Indeed, the experimental K/S value was 9.81, compared to the predicted value of 10.65. As a result, the model suggested in this study has been confirmed and validated. As a result, the optimal dyeing condition was applied to dye fabric samples for evaluating their color fastness and UV protection properties.

3.5 Color Fastness Testing

The dyeing of wool fabrics with *Diospyros mollis Griff.* fruit extract yielded grey-black shade. As shown in Table 2, the dyed samples' color data matched their visual appearance, as the color data with low positive values of a* and b* were located in the red-yellow coordinate of the CIELab color space. Color fastness is the capacity of a colored textile to retain its original hue under normal conditions of use, and it is a requirement for all commercially dyed products. The degree of color change determines the colorfastness. The washing, light, and crocking colorfastness of wool fabrics dyed under the optimal conditions of this study are displayed in Tables 6-7. The color change value was rated as 4 (good). A color staining test was used to further assess color stability. Table 6 shows the degree of color staining on multifiber No.10 (acetate, acrylic, cotton, nylon, polyester, and wool). Each fiber in the multifiber fabric test has polar end groups such as hydroxyl (-OH) or amino ($-NH_2$) groups. As they leaked from the dye samples and contaminated the test medium, these may interact with the phenolic and hydroxyl groups of the dye molecules via hydrogen bond interactions. All of the color staining values in multifiber fabrics were rated as good to excellent (4-5) or good (4). As shown in Table 7, the dyed fabrics have good color fastness to crocking (rated 4) in the dry state but fair to good (rated 3-4) in the

wet state. As predicted, the application of a polar solvent increased the vulnerability of fabrics to color loss upon rubbing, notably when wet. The dyed fabric's color fastness to light was also good (rated 6). In conclusion, all of the fastness properties were rated as good, indicating that this natural dye can be used to dye wools with high color strength as well as satisfactory color fastness.

3.7 UV protection performance

Proper UV rays are beneficial to the human body since they sterilize and stimulate vitamin D synthesis. However, overexposure of skin to UV radiations can cause skin damage and even skin cancer (Rivas et al., 2020).

UV protective textiles are becoming increasingly popular because they provide simple and convenient UV radiation protection. The degree of UV protection depends on a variety of factors such as (1) type of fiber (most natural fibers offer little protection), (2) fabric construction (thicker and denser fabrics offer greater UV protection), (3) fabric preparation (unbleached fabrics offer greater UV protection than desired and bleached fabrics), and (4) fabric's color strength (darker colors increase UV protection) (Vuthiganond et al., 2020). Special UV protection coatings, such as the addition of optical brightening agents or UV absorbers, or plasma treatment with nitrogen or silver, may be applied. (Ayesh et al., 2022; Shahidi, 2014).

Wool fabrics offer insufficient UV protection because their fiber structure lacks carbon-carbon double bonds or UV-absorbing molecules. Some natural dyes with an aromatic ring or a highly polymerized polyphenol structure may function as UV absorbers and provide enhanced UV protection (Pisitsak et al., 2016; Vuthiganond et al., 2020). To investigate the UV protection property of wool fabrics dyed under optimum condition, UPF and UV transmittance parameters are utilized to determine the UV protection efficiency. The percentage transmittance in UV regions measures the amount of UV rays that penetrate the skin and their effects, whereas the UPF rating system measures how well a fabric protects the skin from UV rays. According to the AS/NZS 4399:1996 test method, textile products with a UPF value in the range 15-24 have “Good UV Protection”, 25-39 have “Very Good UV Protection”, and 40-50+ have “Excellent UV protection”. Also, the UV protection property of the dyed fabric is evaluated as good when the UV transmittance is less than 5%. UPF values and percent transmittance of UV-A (315-400 nm) and UV-B (290-315 nm) radiations of untreated and wool fabrics dyed under the optimal conditions were calculated and presented in Table 9. The results demonstrate a significant difference between the untreated and dyed wool fabrics. The untreated wool fabrics had a low UPF of 6.24, resulting in inadequate skin UV protection. As the dyed wool fabrics comprise functional groups that absorb UV radiation, they offer superior UV protection than the untreated wool fabrics, as indicated by the higher UPF values and lower UV transmission percentage (Table 9). The UPF of the dyed wool fabrics also reached the highest (40+) level, demonstrating the enhancing UV protection of the dyed wools.

3.8 Antibacterial Activity

Wool fibers have a high surface-to-volume ratio and the ability to retain moisture, which is conducive to the growth of microorganisms (Alebeid et al., 2020). Figure 8 depicts the antibacterial activity against two key strains of wool fabrics dyed under optimum condition. Firstly, the dyed fabrics were tested against *S.aureus* (Gram-positive) and *E.Coli* (Gram-negative) following AATCC 147. Figure 7 shows the clear zone of inhibition caused by untreated fabrics, dyed fabrics, and tetracycline antibiotics. The dyed fabrics were superior to the untreated fabrics at preventing the growth of microorganisms, despite the fact that tetracycline had a more potent impact. The antibacterial activity was then quantified and calculated as a percentage reduction following the AATCC 100 method as shown in Figure 8. The antibacterial reduction of the dyed wool fabrics against *S.aureus* and *E.Coli* was 90.65% and 93.64%, respectively. Although the dyed fabrics showed good antibacterial activity against both bacteria, the effect was more pronounced against E. coli. Due to the interaction between the positively-charged diospyrol and the negatively-charged bacteria at the cell surface, the antibacterial activity of the dyed sample is greater than that of the untreated sample. This interaction causes extensive changes on the cell surface, leading to cell permeability (Fareed et al., 2022).

Table 5 The proposed optimum dyeing condition

A: pH	B: Dye concentration	C: Temperature	D: Time	predicted *K/S*	actual *K/S*
4	25	88	95	10.65	9.81

Table 6 Color fastness to washing (AATCC 61-2013)

Fastness to	Color change	Color staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Dyed wool	4	4-5	4	4	4-5	4-5	4-5

Table 7 Color fastness to light (ISO 105-B02:1994) and crocking (AATCC 8-2013)

Fastness to	Light	Crocking	
		Dry	Wet
Dyed fabrics	6	4	3

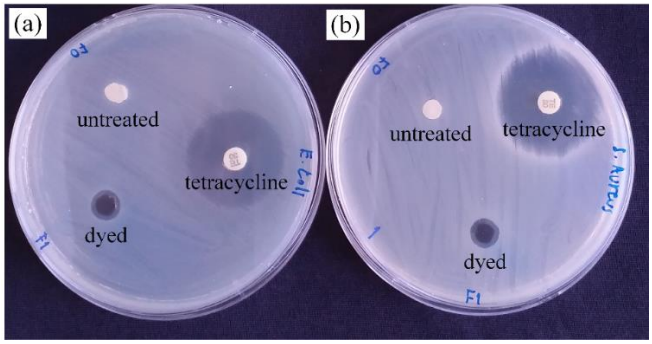

Figure 7 Qualitative analysis for antibacterial activity (AATCC 147): (a) *E.coli* and (b) *S.aureus*

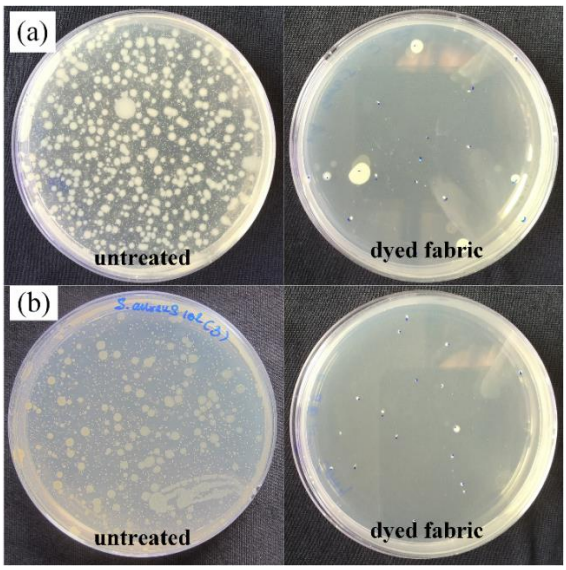

Figure 8 Quantitative analysis for antibacterial activity (AATCC 100): (a) *E.coli* and (b) *S.aureus*

Table 9 UV protection and antibacterial activity

Sample	Calculated UPF	UPF class	%Transmittance		%Reduction	
			UV-A	UV-B	*E.Coli*	*S.aureus*
Untreated	6.24	No class	15.05	9.26	N/A	N/A
Dyed	47.36	Excellent	2.93	1.98	93.64	90.65

4. Conclusion

In the present study, *Diospyros mollis Griff.* fruit extract was applied to the simultaneous dyeing and functionalization of wool fabrics. The diospyrol colorant was successfully extracted and employed to dye wools without the use of hazardous chemicals or metal mordant. RSM along with BBD optimized the dyeing process for the highest color strength. The optimal condition was found and confirmed to be pH 4, dye concentration of 25 g/L, temperature of 88 °C, and time of 95 min. The finished fabrics had a black hue with a K/S value greater than 9, and their color fastness against washing, light, and crocking was rated as good to excellent (ratings > 4). The dyed wools had good antibacterial activity against both *E.coli* and *S.aureus* (bacterial colony reduction > 90%), with *E.coli* being more pronounced. Additionally, the UPF reached the highest level (40+), demonstrating their superior UV protection. Thus, an aqueous fruit extract of *Diospyros mollis Griff.* has potential textile applications for antibacterial and anti-UV functionalization, as well as simultaneous coloring of textile fibers.

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