OPTIMIZATION OF HEMP FABRIC NATURAL DYEING IN SUPERCRITICAL CARBON DIOXIDE MEDIUM BY RESPONSE SURFACE METHODOLOGY

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This study explores the dyeing of hemp fabric, a natural cellulosic material, using henna as a natural dye in a supercritical carbon dioxide ($scCO_2$) medium. Given the significant environmental impact of conventional textile finishing, the research aims to provide an eco-friendly alternative to synthetic dyes. Response surface methodology (RSM) was applied to optimize dyeing conditions, focusing on temperature, pressure, and time. The dyed samples were evaluated in terms of color fastness properties to assess the dye uptake and performance. The results showed that efficient dyeing was achieved without water, with maximum color strength (K/S value) at 120 °C, 21 MPa, and 90 minutes. The experimental K/S value closely matched the predicted value, validating the model's accuracy. Overall, the study demonstrated that natural dyeing of hemp in $scCO_2$ is feasible and sustainable, offering a waterless and environmentally friendly alternative for textile coloration.

Keywords: $scCO_2$ dyeing, cellulose, hemp fabric, natural dye, henna, response surface methodology

INTRODUCTION

Textile finishing processes involve the use of various chemicals, leading to significant water and energy consumption.[1] These processes also result in the production of substantial amounts of colored wastewater, making water pollution a major environmental concern.[2] The issue of water pollution is exacerbated by the growing global population.[3] In response to these challenges, researchers have explored the use of waterless dyeing technology with supercritical carbon dioxide ($scCO_2$) to mitigate water pollution in the dyeing processes.[4] This environmentally friendly dyeing technology employs non-toxic carbon dioxide, which can be recycled.[5] Drying and wastewater treatment are not required with the energy- and money-efficient $scCO_2$ dyeing method. 90% of the CO_2 and leftover dye may be recycled and used again. Because $scCO_2$ has a high diffusivity and a low viscosity, it can spread dye molecules and swell fibers, which is advantageous to the process. Additionally, by varying the pressure and temperature, dye can be readily separated from $scCO_2$. Therefore, $scCO_2$ dyeing is a sustainable, green, and eco-friendly process.[6] In contrast, in traditional cellulosic fiber dyeing, high volumes of effluents pose a threat to the environment.[7] After dyeing cotton fabric, the dye house effluent is thought to contain up to ~1000–2000 tonnes of unfixed dye.[8]

The process of waterless dyeing in a $scCO_2$ medium was employed for coloring synthetic fibers, particularly polyester, utilizing disperse dyestuffs. However, the dyeing of natural fibers using this technology presents challenges and is still under development.[9,10] Because of the limited disruption of hydrogen bonds on natural fibers within this environment, dyestuffs struggle to penetrate the fibers, resulting in ineffective dyeing.[11]

Hemp, a plant with a rich history of cultivation, belongs to the *Cannabinaceae* family. It is a sturdy, annual plant.[12,13,14] Hemp is considered more environmentally friendly compared to widely used cotton and synthetic fibers.[15] Its eco-friendliness is attributed to its reduced need for pesticides and herbicides during growth.[16] In addition, its growing conditions require less space and less water compared to cotton. Rainwater is sufficient for the growth of hemp, so there is no need for extra irrigation.[19,20]

Moreover, hemp fiber offers high absorbency, excellent thermal properties, UV radiation protection, and high strength, making it a versatile and sustainable choice for clothing.[13,17,18] With its excellent capillarity effect, hemp fiber has very good moisture absorbing and breathing performance.[21]

In the textile industry, synthetic dyestuffs are commonly utilized due to their cost-effectiveness and the high colorfastness they provide.[22,23] However, the detrimental environmental impacts of synthetic dyes have raised significant concerns.[24] In light of escalating environmental and health issues caused by pollution, there is a growing interest in the use of natural dyes as an eco-friendly and non-toxic alternative to synthetic dyes.[25,26,27] In their study, Wu *et al.*[5] grafted alkyl and hydroxyalkyl onto cotton, wool, and silk fabrics, subsequently dyeing them with a natural dyestuff, an alizarin derivative, in a supercritical carbon dioxide ($ScCO_2$) medium. The fabrics treated with hydroxyalkyl exhibited superior dyeing performance in this medium, and their fastness values were also higher.[5] In another investigation, Schmidt-Przewozna and Roj dyed silk and linen fabrics in a supercritical carbon dioxide environment using *Rubia tinctorum* natural dyestuff. According to their findings, fabrics dyed in this environment displayed more vibrant colors.[28]

Henna, also known as lawsone or hennotannic acid, is a natural dye.[29,30] Its key attributes include its non-toxic nature and environmental friendliness.[29] However, henna's affinity for natural fibers is relatively low because of the apolar structure of henna and the polar structure of cellulosic fibers. Consequently, dyeing with henna often involves the use of mordants, as reported in the literature.[31-34] Elevated dyeing temperatures cause the fibers to swell and their structure to open. Simultaneously, higher temperatures increase the solubility of henna dye and decrease its particle size. These factors collectively enhance dye absorption by the fibers.[29]

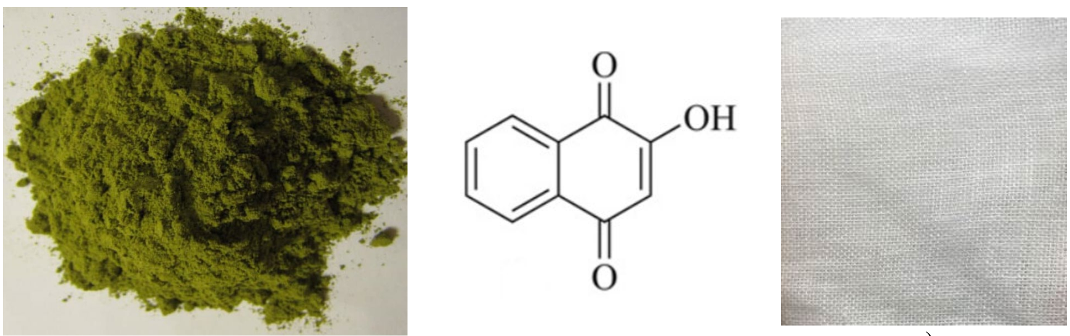
Response surface methodology (RSM) design is commonly adopted by researchers due to its cost-effectiveness in extracting complex information and its capacity to save time and resources for analysis.[35] RSM, based on three-level factorial designs, optimizes the number of experiments to investigate interactions between the parameters in experimental studies.[36,37]

To the authors' knowledge, in the existing literature, no studies address the dyeing of hemp fabrics using natural dyes in a supercritical carbon dioxide medium. In this study, hemp fabric was dyed with henna natural dyestuff under conditions determined by using the response surface methodology design. The results obtained were subsequently analyzed and interpreted. Despite the inherent challenges and low affinity of henna for natural fibers, we selected supercritical CO_2 as the dyeing medium for its environmental benefits, enhanced dye penetration capabilities, and the potential for optimized dye–fiber interactions through precise control of temperature and pressure conditions.

EXPERIMENTAL

Materials

In this study, 100% plain woven hemp fabric (120 g/m², 18 ends/cm warp density, 16 picks/cm weft density) and henna (*Lawsonia inermis* L., Ardakan, Iran), in powder form, as a natural dyestuff, were utilized.



a) b) c)

Figure 1: a) Henna in powder form; b) Structure of lawsone, which is the major component of henna;[29] c) Hemp fabric

The hemp fabric, having undergone the preparatory treatments described below, was subjected to waterless dyeing processes using a Rapid Xiamen Model H-12 oil bath dyeing machine (Fujian, China). The structure and appearance of henna are presented in Figure 1.

Methods

The hemp fabric was subjected to a desizing process prior to dyeing. The treatment was carried out in an aqueous bath containing 2 g/L non-ionic wetting agent and 2 g/L sodium carbonate at 95 °C for 30 minutes with a liquor ratio of 1:20. After treatment, the samples were thoroughly rinsed with distilled water and air-dried at room temperature.

Subsequently, 100% hemp fabrics were dyed in a supercritical carbon dioxide medium at determined temperatures, pressures, and times without using any water. Waterless dyeing was performed using the Rapid Xiamen Model H-12 oil bath dyeing machine from DyeCOO (the Netherlands). In the first stage of the dyeing process, the hemp fabric was wrapped around a beam and placed into dye tubes made of stainless steel, with an internal volume of 290 mL. Then, 1 g of dye was added to the tube and the tube's lid was closed (Step 1). After preparing the tube, the dyeing tube was kept in a deep freezer for at least 15 minutes to facilitate the filling of carbon dioxide gas into the tube (Step 2). The density (d) of CO_2 gas was calculated from the NIST Chemistry WebBook, considering the temperature and pressure values according to the experimental conditions (Step 3). The amount of CO_2 gas (g) was calculated using the formula d = m/V. In the final step, the samples were placed in the device.[38]

A visual representation of the dyeing process is presented in Figure 2. Figure 3 shows the DyeCOO oil bath machine and dyeing tube.

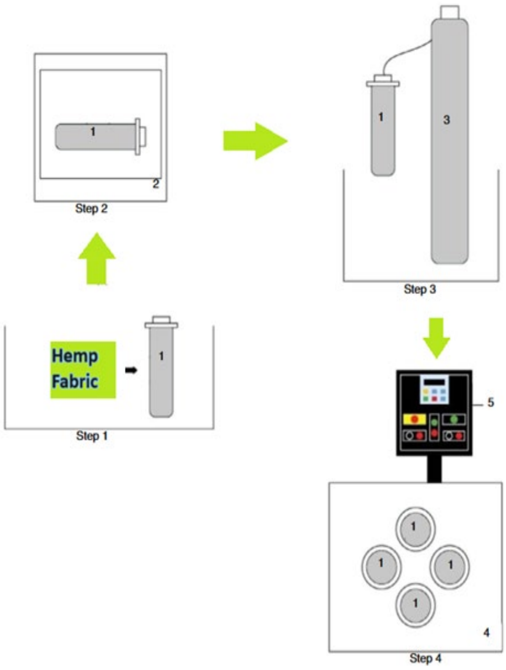


Figure 2: ScCO$_2$ dyeing system (stainless steel container (1), freezer (2), CO_2 cylinder (3), dyeing machine (4)[38]

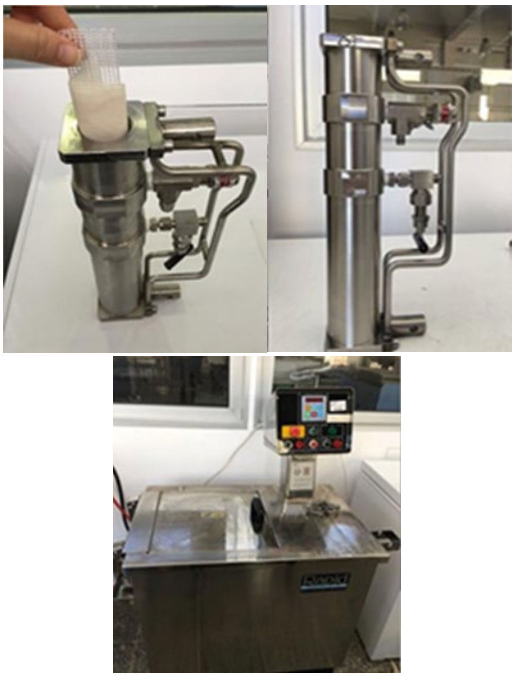


Figure 3: DyeCOO oil bath machine and dyeing tube[39]

Table 1
Dyeing parameters

Factor	Lower limit	Upper limit
A - Temperature (°C)	60	120
B - Pressure (MPa)	16	24
C - Time (min)	60	90

Table 1 presents the selected pressure, temperature, and duration values determined based on the ranges commonly chosen by various researchers[11,39,40,41] in their studies on cellulose fibers, with 1 g of dye prepared and 5 g of fabric used. Color measurements of the dyed samples were conducted using a Konica Minolta CM3600D model spectrophotometer and analyzed employing the Box-Behnken design methodology (Design Expert software by Stat-Ease, Minneapolis, MN). As indicated in Table 1, the results were assessed with consideration to the influence of three key factors. The factor levels were represented as follows: -1 for "low", 0 for "central point" or "middle", and 1 for "high".[42] In Equation (1), we applied the model to the experimental data to identify the significant model terms. The quadratic response model, encompassing all linear terms, square terms, and linear by linear interaction terms, can be expressed as follows:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_{ii}^2 + \sum \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

where β_0 represents the constant, β_i signifies the slope or linear effect of the input factor x_i, β_{ij} denotes the linear by linear interaction effect between the input factors x_i and x_j, and β_{ij} is the quadratic effect of the input factor x_i.[43,44]

In the process of supercritical dyeing, the impregnation yield is typically assessed through the color strength (K/S) value, which signifies the color depth of the dyed fabric. This value is directly associated with the concentration of dye present on the material. K/S values can be determined from spectrophotometric measurements in reflectance mode by employing the Kubelka-Munk function:[45,46,47]

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

where K/S represents the ratio between the absorbance and the scattering coefficient of the tested fabric, while R denotes its reflectance at the dye's peak wavelength.

Characterisation tests

Dye solubility

The dye's solubility can significantly affect the color intensity of the fabric dyed in $scCO_2$. A sample of 0.1 g of henna was first weighed using an electronic balance. After that, the material was introduced into the staining tube. A high pressure pump was used to pressurise the staining tube. The staining tube was held in the apparatus for an hour at 110 °C and 26 MPa of pressure. To recycle the CO_2, the relief valve was gently opened. The staining tube was opened and the rest of the sample was weighed once the pressure was lowered. The following formulas were used to determine the solubility:

$$n_{dye} = (0.1000 - m_{dye}) / M_{dye} \quad (3)$$

$$n_{CO_2} = (\rho_{CO_2} \times V_{CO_2}) / M_{CO_2} \quad (4)$$

$$S = n_{dye} / n_{CO_2} \quad (5)$$

where ndye and nCO_2 represent the amounts of dye and carbon dioxide in moles, respectively; S is the solubility of henna in $scCO_2$; MCO_2 is the molecular weight of carbon dioxide, while Mdye corresponds to the average molecular weight assumed based on the total henna powder used, acknowledging that henna is a mixture of various compounds with lawsone being the main coloring component; mdye is the mass of the residual sample (g); ρCO_2 is the density of $scCO_2$ at 26 MPa and 110 °C (g/cm³); and VCO_2 is the volume of $scCO_2$ in the dyeing autoclave (mL).

Methylene blue test

Oxidation of the cellulose in natural fibers results in the formation of carbonyl and carboxyl groups, making the fibers more amenable to dyeing with cationic dyes and increasing their carboxyl group content.[48] Consequently, the presence of oxycellulose becomes evident within the natural fiber. This potential damage can be assessed using methylene blue cationic dye. Natural fibers affected by such damage can be dyed with a 0.1% concentration of methylene blue cationic dye at temperatures ranging from 60 to 100 °C for 5 minutes, or in cold water for 20 minutes.[49] Hemp fabrics (untreated, $scCO_2$ treated) were ultimately dyed using 0.1% methylene blue cationic dye (Merck) at 75 °C for 5 minutes. In this way, the intensity of the fabric's blue hue, or its color yield (K/S), directly correlates with the extent of oxycellulose formation.[50]

Color fastness and tensile strength tests

Multifiber fabric was utilized for washing durability measurements, to comprehensively assess the resistance of the tested samples to diverse washing conditions. Washing fastness tests were conducted using a 412 NB HT Model washing fastness test device in accordance with the ISO 105-C06:2010 standard, while rubbing fastness tests were performed using the James Heal Crockmeter test device following the ISO 105-X12:2016 standard. The results of the fastness tests were assessed using a grey scale. Perspiration fastness of the dyed fabrics was evaluated according to ISO 105-E04 standard, using both acidic and alkaline perspiration solutions. The samples were treated at 37 ± 2 °C for 4 hours, and the staining and color change were assessed using the grey scale.

Tensile strength tests were carried out utilizing a Shimadzu AG-X Plus Model (Kyoto, Japan), in accordance with the TS EN ISO 13934-1 standard.

RESULTS AND DISCUSSION

Box Behnken analysis

The experimental design and K/S values of the dyed samples, determined using the Box-Behnken design method, were presented in Table 2. Three distinct models, namely linear, quadratic, and cubic, were employed to identify the most suitable model for representing the relationship between the variables.

The results obtained, as shown in Table 3, examined the relationship of different model types with the same independent variable. The quadratic model is known for attempting to establish a second-order relationship. Notably, the Adjusted R^2 value of this model is quite high, indicating a stronger explanatory capacity for the dependent variable. The positive Predicted R^2 suggests that this model effectively describes the dependent variable. Among the three models considered, the quadratic model exhibits the highest explanatory power. The adequacy of the model was further validated through ANOVA analysis, as shown in Table 4.

These data present the results of a multiple regression analysis that assesses the statistical significance and the capacity of various independent variables and interactions to account for the dependent variable. The findings reveal that independent variables A, AB, AC, A^2, and B^2 exhibit substantial and highly explanatory power concerning the dependent variable. These factors were statistically significant at the $p < 0.05$ level, and their effects were significant at the 95% confidence level. Conversely, independent variables B, C, BC, and C^2 display limited explanatory power and lack statistical significance.

Table 2
Experimental design

Run	Factor 1: Temperature (°C)	Factor 2: Pressure (MPa)	Factor 3: Time (min)	K/S	Colour
1	120	20	90	1.85	
2	90	24	60	0.90	
3	90	20	75	1.05	
4	120	20	60	1.25	
5	90	16	60	0.95	
6	90	20	75	1.06	
7	60	24	75	0.82	
8	90	24	90	1.11	
9	90	20	75	1.04	
10	90	16	90	0.85	
11	60	20	60	1.38	
12	90	20	75	1.05	
13	90	20	75	1.06	
14	120	16	75	1.34	
15	60	16	75	1.20	
16	120	24	75	1.37	
17	60	20	90	1.12	

Table 3
Design models

Source	Sequential p-value	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	0.3004	0.2380	0.0621	-0.5561	1.54	
2FI	0.2379	0.4913	0.1860	-1.4518	2.43	
Quadratic	0.0006	0.9525	0.8913	0.2434	0.7496	Suggested
Cubic		0.9997	0.9989			Aliased

Table 4
ANOVA analysis and statistical parameters of the model

Source	Sum of squares	df	Square mean	F-value	p-value	
Model	0.9437	9	0.1049	15.58	0.0008	Significant
A	0.2080	1	0.2080	30.91	0.0009	
B	0.0025	1	0.0025	0.3641	0.5653	
C	0.0253	1	0.0253	3.76	0.0936	
AB	0.0420	1	0.0420	6.25	0.0411	
AC	0.1849	1	0.1849	27.48	0.0012	
BC	0.0240	1	0.0240	3.57	0.1007	
A^2	0.3517	1	0.3517	52.26	0.0002	
B^2	0.1058	1	0.1058	15.72	0.0054	
C^2	0.0147	1	0.0147	2.18	0.1835	
R^2	Adjusted R^2	Adeq. Precision	%CV			
0.9525	0.8913	16.3909	7.19			

In summary, the model provides a significant explanation for the dependent variable. To enhance the response surface model, statistically insignificant terms ($p > 0.05$) were eliminated from the quadratic equation, excluding variables that marginally contributed to the model's effectiveness.[51] Equation 2 represents the refined model that includes all significant terms derived from the original quadratic equation:

$$K/S = 1.05+0.1613A-0.0175B+0.0563C+0.1025AB+0.2150AC+0.2890A^2-0.1585B^2 \quad (6)$$

As shown in Table 4, the R^2 value exceeds 0.08, signifying the successful creation of an accurate model.[52] While the predictive ability of a model is often assessed through the R^2 value, it can be misleading as the number of terms increases. Therefore, it should be compared to the adjusted R^2 value. Specifically, if the R^2 value and the adjusted R^2 value are closely aligned, it indicates that the model includes meaningful terms and offers a good fit.[53] In this context, the obtained R^2 value is 0.9525, which aligns closely with the adjusted R^2 value of 0.8913, affirming that the model incorporates meaningful terms and fits the data well. The fit sensitivity, measuring the signal-to-noise ratio, boasts a value exceeding 4 (16.3909), denoting a significant and robust signal within the model.[54] Consequently, this model can be effectively employed in design processes, offering valuable insights. The coefficient of variation (%CV), with a value of 7.19, reveals the extent of data dispersion. It was noteworthy that the literature emphasized that the %CV should be below 10%.[55]

Creating a normal probability plot for residuals provides a valuable method to assess whether the data follows a normal distribution.[56,57] The normality assumption was assessed by creating a normal probability plot of the residuals, as shown in Figure 4 (a). The data points on the plot closely align with the straight line. The interpretation of this diagram indicates that the residuals exhibit a close-to-normal distribution. Additionally, in Figure 4 (b), the predicted response generated through RSM was compared to the actual response to validate the accuracy of the predictions. As illustrated in Figure 4 (b), the predicted values align well with the actual values, confirming the reliability of the predictions.

Effect of various parameters on K/S values

Based on the calculation method provided above, the solubility of the dye in the $scCO_2$ medium was determined to be 5.757×10^{-4}. This value was found to be higher than the solubility values of other natural dyes, such as alizarin and curcumin, in $scCO_2$ medium.[5,9]

The parameters influencing the color durability of dyeing hemp fibers with henna in $scCO_2$ medium were illustrated in Figure 5. It was found that temperature alone is an effective factor ($p = 0.0009$). As the temperature increases, K/S shows a proportional increase. Dyeing at 120 °C resulted in the highest K/S value. In a study by Zaghloul *et al*. on dyeing cotton fibers, a natural fiber akin to hemp, in $scCO_2$ medium, it was also observed that K/S increased with rising temperatures.[41] Higher temperatures increased the kinetic energy of the dye molecules, creating larger pores in the fabric. This led to increased swelling and reduced dye reactivity. This situation aligns with another study[58] on dyeing hemp fiber with natural dyestuffs in a conventional setting. Schneider and coworkers noted that the solubility of natural dyes increases with temperature.[59]

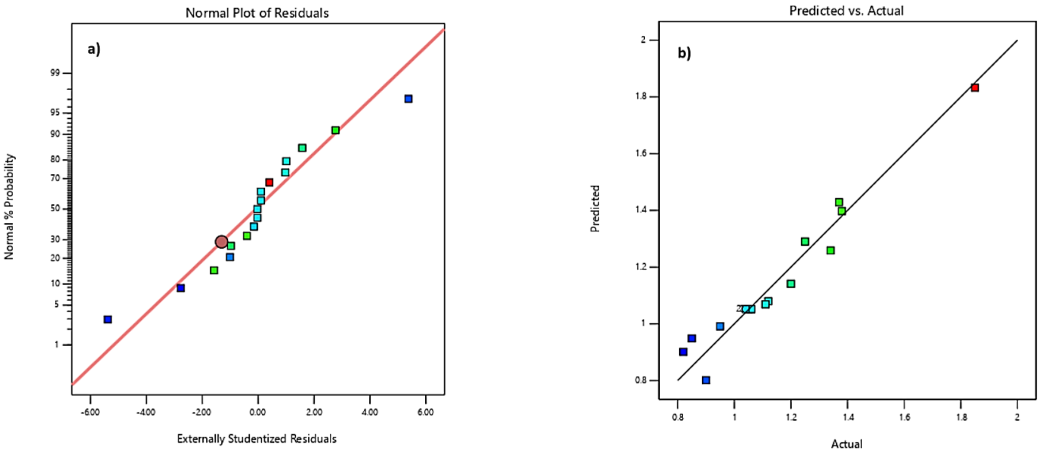


Figure 4: Normal (a) and predicted (b) plots of residuals

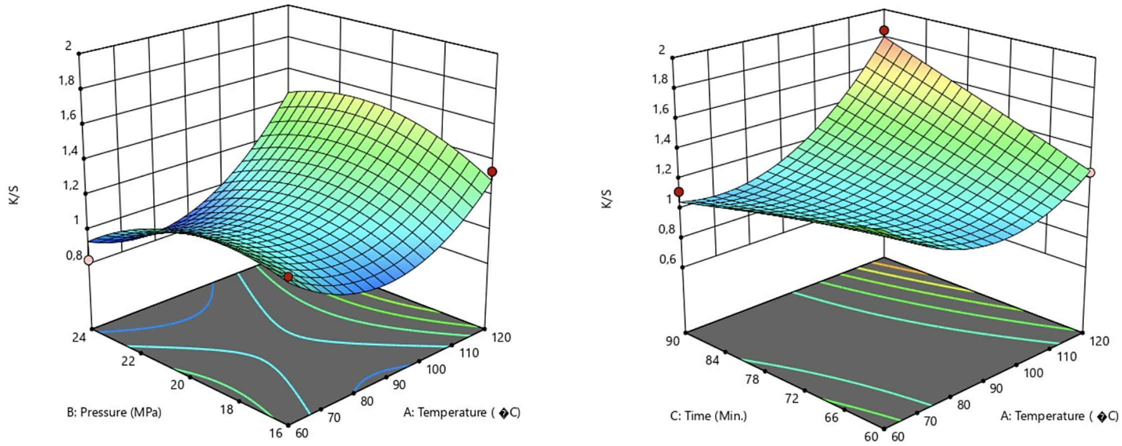


Figure 5: 3D Response surface plots for (a) the effects of temperature and pressure on K/S, and (b) the effects of temperature and time on K/S

The pressure parameter alone did not cause a significant change ($p = 0.5653$). However, dyeing in $scCO_2$ medium, within the 16-22 MPa pressure range, showed subtle differences in color variation. It was reported that, in the system used, the density of pure supercritical carbon dioxide increases with pressure at a constant temperature, facilitating the dissolution of dyestuff molecules. This, in turn, allows more dissolved dye molecules to be adsorbed onto the fiber surface and, subsequently, diffuse into the amorphous regions of the fiber.[10] Nevertheless, a decrease in K/S values is observed beyond 22 MPa pressure, a phenomenon explained in the literature as an outcome of the Nernst thermodynamic equation. According to this equation, the solubility in the liquid phase increases with rising pressure, potentially affecting the distribution within the fiber and the dyeing process.[60,61] While the time parameter was not significant on its own ($p = 0.0936$), a temperature-dependent increase was displayed. K/S values rose with longer time durations in dyeing processes conducted in $scCO_2$ medium at 120 °C. This observation aligns with similar findings in the literature for dyeing of cotton[62] and ramie[63] fibers in $scCO_2$ media.

In addition to pressure, temperature, and duration parameters, it was hypothesized that hemp fibers, similarly to cotton, might undergo oxycellulose formation in $scCO_2$ medium, potentially affecting K/S values. To investigate this, a methylene blue test was conducted, as described in the methodology section. The results showed that the untreated hemp fabric had a K/S_{sum} value of 151.95, while the fabric exposed to $scCO_2$ conditions (21 MPa, 120 °C, 90 min) had a K/S_{sum} value of 183.17. This indicates that the increase in K/S values is due to the formation of oxycellulose in hemp fibers, when subjected to $scCO_2$, which enhances the dye uptake.

Optimization and verification of the model

All the parameters of dyeing hemp fabric in supercritical CO_2 medium were assessed. The RSM model applied provided 57 solutions to attain the maximum K/S value, and the predicted and experimental responses are presented in Table 5. Color measurements of the dyed samples were carried out with reference to the undyed fabric, and the results are expressed in terms of CIE L*, a*, b*, and ΔE values. As shown in Table 5, the dyed sample exhibited a decrease in L* (–7.83), indicating a darker appearance compared to the undyed fabric, while the positive a* (3.808) and b* (15.474) values reflect shifts toward red and yellow hues, respectively. The overall color difference, ΔE, was 17.40, confirming a significant perceptible color change due to the dyeing process.

The observed higher K/S value for the sample was attributed to the specific dyeing conditions and parameters employed in the experiment. These conditions played a significant role in achieving the remarkably strong color strength. Figure 6 displays both the untreated and dyed versions of the hemp fabric, revealing that the dyestuff is uniformly distributed across the fabric's surface.

Table 5
$K/S_{predicted}$ and $K/S_{experimental}$ values in optimization

Temperature (°C)	Pressure (MPa)	Time (min)	$K/S_{Predicted}$	$K/S_{Experimental}$
120	21	90	1.815	2.323
Experimental sample	DL*	Da*	Db*	ΔE
	-7.83	3.808	15.474	17.40

Untreated fabric ScCO2 dyed fabric (120 °C, 21 MPa, 90 min)

Figure 6: Images of hemp fabric

Table 6
Fastness properties of hemp fabric dyed under optimum conditions

Optimized conditions	Washing fastness						Rubbing fastness		Perspiration fastness	
120 °C	Wool	Acrylic	Polyester	Polyamide	Cotton	Acetate	Dry	Wet	Acid	Alkali
21 MPa 90 min	5	5	5	4-5	4-5	4-5	4-5	4-5	4-5	4-5

Table 7
Maximum force (N) values of hemp sample

Samples	Maximum force (N)
Untreated fabric	366.286
$scCO_2$ dyed fabric	288.244

The washing and rubbing fastness results from the experimental study were detailed in Table 6. The findings from the experimental study reveal that the washing fastness scores range between 4 and 5 on the gray scale, which is considered commercially acceptable. This suggests a commendable color retention following washing. Additionally, the rubbing fastness results, falling within the range of 4-5, indicate a substantial resistance to color transfer or fading when the fabric was subjected to abrasion.

The maximum force values for both untreated and dyed samples are presented in Table 7. A review of the results indicates a slight reduction in the maximum force of the samples after the dyeing process. This minor strength loss is considered commercially acceptable and has been consistently reported in the literature by researchers conducting dyeing studies in supercritical carbon dioxide ($scCO_2$) medium.[47,64,66]

CONCLUSION

In conclusion, this study demonstrated successful dyeing of hemp fabric in supercritical CO_2 ($scCO_2$) medium. The process was optimized using the response surface methodology, specifically the Box-Behnken design, to identify the key parameters affecting the dyeing efficiency. Three critical factors – temperature, pressure and time – were found to significantly influence the dyeing performance in the $scCO_2$ medium. The optimal conditions predicted by the Box-Behnken design were 120 °C, 21 MPa, and a 90-minute duration, under which the experimental K/S value of the dyed sample exceeded the predicted value, confirming the successful dyeing of hemp fabric with henna as a natural dyestuff.

Furthermore, the results of the fastness and mechanical tests indicated satisfactory performance, while the relatively low K/S values observed in hemp fibers were attributed to the formation of oxycellulose under $scCO_2$ conditions. Future studies will focus on enhancing dye uptake by optimizing dyeing parameters, exploring alternative pretreatment methods, and employing suitable additives.

This research highlights the effectiveness of $scCO_2$ technology as an environmentally friendly and efficient alternative for dyeing natural, sustainable fibers such as hemp. The innovative waterless dyeing approach minimizes chemical usage and reduces environmental impact and resource consumption, offering a sustainable solution for the textile industry.

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