sustainability

MDPI

Article

Sustainable Dyeing of Wool and Silk with *Conocarpus erectus* L. Leaf Extract for the Development of Functional Textiles

Tayyaba Nadeem, Kashif Javed, Faiza Anwar, Mumtaz Hasan Malik and Asfandyar Khan *

Department of Textile and Apparel Science, School of Design and Textiles (SDT), University of Management and Technology, Lahore 54770, Pakistan; tayyabamikail881@gmail.com (T.N.); kashif.javed@umt.edu.pk (K.J.); faiza.anwar@umt.edu.pk (F.A.); sdt.dean@umt.edu.pk (M.H.M.)
* Correspondence: asfandyarkhan100@gmail.com; Tel.: +92-31-6194-1611

Abstract: Natural dyes derived from plants offer a sustainable alternative to synthetic dyes for textile coloration. This study examined the extraction of natural dyes from *Conocarpus erectus* L. leaves and their application on wool and silk fabrics. Aqueous extraction in an alkaline medium was used to obtain dyes from raw leaves, which were then applied to pre-mordanted silk and wool fabrics by applying the ultrasonic-assisted exhaust dyeing method. The dyed fabrics were evaluated for color strength (K/S) and CIELAB color coordinates. The color fastness (washing, rubbing, and light), ultraviolet protection factor, mosquito repellency, and antibacterial activity were established using standard testing protocols. The surface morphologies of silk and wool were examined using scanning electron microscopy. Interestingly, the dyed fabrics displayed good color strength and color fastness properties. Moreover, the dyed wool samples revealed satisfactory antibacterial activity against Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) in both qualitative and quantitative assessment methods, good ultraviolet protection in terms of UPF, and good mosquito repellency against Aedes aegypti. This study for the first time presented the application of a medicinal plant (*Conocarpus erectus* L.) in the field of textile dyeing and finishing. Hence, the use of *Conocarpus erectus* L. leaf dyes offers significant results on wool and silk fabrics and contributes to sustainable functional textile production.

Keywords: sustainable dyeing; mosquito repellency; antibacterial activity; ultraviolet protection factor

Citation: Nadeem, T.; Javed, K.; Anwar, F.; Malik, M.H.; Khan, A. Sustainable Dyeing of Wool and Silk with *Conocarpus erectus* L. Leaf Extract for the Development of Functional Textiles. *Sustainability* **2024**, *16*, 811. https://doi.org/10.3390/su16020811

Academic Editors: Slavenka Petrak and Martinia Ira Glogar

Received: 5 December 2023
Revised: 9 January 2024
Accepted: 12 January 2024
Published: 17 January 2024

1. Introduction

Natural dyes refer to colorants derived from organic materials including plants and animals. They have been used since ancient times to impart color to textiles, leather, paper, food, and other materials [1]. In contrast to synthetic dyes, which are chemically synthesized from petrochemical sources, natural dyes are obtained from renewable resources making them more sustainable and eco-friendly [2]. The earliest evidence of textile dyeing dates back to civilizations like Egypt, China, India, and Greece that developed expertise in producing colors from diverse natural sources [3]. Despite the dominance of synthetic dyes since the late 19th century due to their cost, consistency, and fastness properties, natural dyes have witnessed a resurgence in recent years. Growing awareness about the toxicity and environmental impact of synthetic dyes has led to increased demand for sustainable natural colorants [4]. Consumers are also seeking uniqueness, artisanal quality, and cultural connections associated with natural dyes. Their non-toxic, non-allergic, and soothing qualities appeal to environmentally and health-conscious buyers [5]. Natural dyes can be derived from two main sources:

Plant Dyes: Obtained from various parts of plants such as leaves, flowers, fruit, bark, and roots. Key examples include indigo (blue) from *Indigofera tinctoria* L., madder (red) from *Rubia tinctorum* L., turmeric (yellow) from *Curcuma longa* L., and henna (orange) from *Lawsonia inermis* L. [6].

Animal Dyes: Derived from insects and shellfish, e.g., cochineal (red) from cochineal insects and Tyrian purple (violet) from sea snails. They produce luxury colors but limited supply [7,8].

Compared to synthetics, the limitations of natural dyes include lower color consistency, weaker colorfastness properties, and higher cost. However, renewable sourcing, biodegradability, and lack of harmful effluents make them an eco-friendly and sustainable choice [9]. Natural dyeing techniques like fermentation, botanical prints, and natural mordanting allow the creation of novel shades in an environmentally low-impact manner. There has been growing research interest in discovering new alternative sources of natural dyes as well as improving extraction and application techniques [10] Natural dyes from different botanical sources have been examined for their potential in textile coloration as well as imparting functional properties to fabrics [11]. Plant-based dyes containing bioactive compounds [12,13] can provide fabrics with antibacterial, UV protective, antioxidant, and other beneficial effects in addition to coloration [5]. This study focuses on the extraction of natural dyes from the leaves of the *Conocarpus erectus* plant and their application to wool and silk textiles. *Conocarpus erectus* is a genus of flowering plants and shrubs belonging to the *Combretaceae* family. It has two main species—*Conocarpus erectus* (buttonwood) and *Conocarpus lancifolius* (swamp tea) that grow across tropical and subtropical regions [14]. Previous research has shown the presence of phenolic compounds like flavonoids, tannins, gallic acid, and anthocyanins in *Conocarpus erectus* leaves (as shown in Figure 1), which can serve as natural dyes [15]. These phytochemicals are also known to have antimicrobial, antioxidant, and anti-inflammatory bioactivities [16]. Hence, *Conocarpus erectus* leaf [17] dyes have the potential to impart functional properties, in addition to an eco-friendly coloration for textiles.

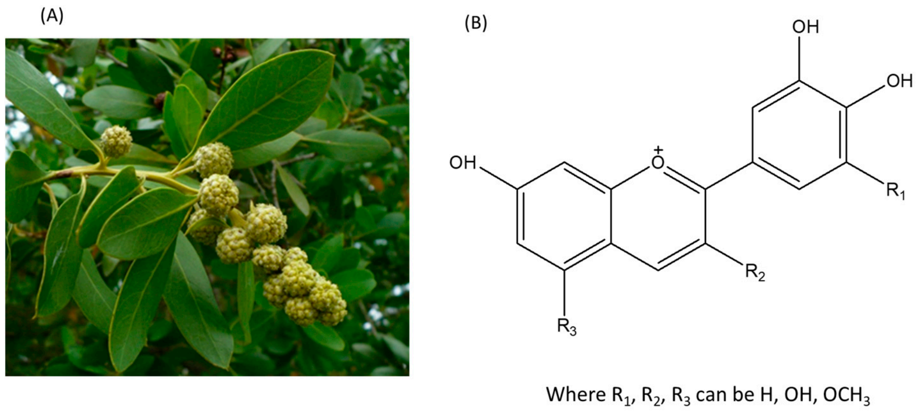

Figure 1. Fruit and leaves of *Conocarpus erectus* plant [17] (**A**) and chemical structure of anthocyanins found in *Conocarpus erectus* plant leaves extract (**B**).

Various solvents like water, ethanol, and methanol can be used for extracting dyes from plant materials based on the solubility of their colorant compounds [18]. For water-soluble dyes, aqueous extraction is a common green technique that avoids the use of organic solvents. Alkali like sodium hydroxide is sometimes added to aid dissolution in water [19]. The dye extract can then be applied to fabrics by techniques including dyebaths, printing, or surface coating. Mordants help fix dyes to textile fibers and enhance fastness. Metal salts like potassium aluminum sulfate (alum), ferrous sulfate, stannous chloride, and copper sulfate are commonly used [20]. Ultrasonication has provided rapid and uniform distribution of dyes onto textile fibers while eliminating the need for high temperatures or other harsh chemicals. The cavitation effects of ultrasound waves enhanced dye diffusion by breaking down aggregated dye particles [21]. Sonication also avoided the need for constant mechanical stirring [22]. Sonication dyeing produced more uniform coloration and faster dye penetration into the fabrics compared to conventional dyebath methods.

This research investigates the aqueous extraction of dyes from *Conocarpus erectus* leaves and their application on wool and silk fabrics via pre-mordanting and sonication techniques. The effects of pH on the color strength and functional properties of dyed fabrics are examined. The fastness, antibacterial activity, UV protection, and mosquito-repellency properties of the dyed textiles are tested. This study provides insights into the suitability of *Conocarpus erectus* leaf dyes as renewable colorants for eco-friendly multifunctional textiles. The key novelty of this work is the use of *Conocarpus erectus* leaf extracts as renewable and sustainable colorants for dyeing wool and silk textiles. To the best of our knowledge, this is the first scientific report on the application of *Conocarpus erectus* dyes for the functionalization of high-value protein fabrics.

2. Materials and Methods

2.1. Materials

The plain weave silk fabric with 78 ends/inch, 70 picks per/inch, and 50 g/m^2 surface density and wool with 28 ends/inch, 32 picks/inch, and 85 g/m^2 areal density were used for this study and purchased from a local market in Lahore, Pakistan. *Conocarpus erectus* leaves were hand picked from the botanical garden of the University of Management and Technology (UMT), Lahore, Pakistan. NaOH (0.25%), acetic acid, and copper sulfate (mordant) were purchased from Sigma Aldrich Chemical Pvt. Ltd. Lahore, Pakistan. All chemicals were used as received without any further purification. Distilled water was used throughout this study.

2.2. Methods

2.2.1. Dye Extraction

Fresh leaves from mature *Conocarpus erectus* plants were collected in July and washed thoroughly with water to remove dust and debris. The leaves were dried under shade at ambient temperature for 48–72 h. The dried leaves were cut into small pieces and 10 g of the powdered leaves were added to a 1000 mL beaker and filled with distilled water. The beaker was placed on a magnetic hot plate with continuous stirring. Sodium hydroxide was added at 1 g/L concentration as an alkali adjuvant to aid extraction [19]. The mixture was boiled at 100 °C for 60 min to facilitate the leaching of dye compounds into the water. The dye extract solution was filtered while hot through a muslin cloth followed by Whatman No. 1 filter paper. The filtrate constituted the aqueous dye extract for application on textile fabrics such as wool and silk.

2.2.2. Mordanting

Wool and silk fabric samples were pre-treated with mordants before the dyeing process. Mordants help fix natural dyes on fabrics by forming a coordination complex and improving their adherence. Copper sulfate was used as the mordant in 0.2% concentration on the weight of fabric (o.w.f.). The mordanting bath was prepared by dissolving copper sulfate in 200 mL of distilled water; 1 g each of wool and silk fabric was treated in the mordant solution for 45 min at 60 °C with occasional stirring. The mordanted samples were rinsed with distilled water to remove the unfixed mordant from the surface. Pre-mordanting of fabrics was chosen to allow sufficient time for the coordination of complex formation between mordant metal ions and fiber functional groups before dyeing. Pre-mordanting also enhances dye–metal–fiber interactions for improved fastness properties [22,23]. Pre-mordanting is considered the best among all mordanting techniques, which is why we applied it in this research work.

2.2.3. Sonication Dyeing

The ultrasonic-assisted dyeing of wool and silk fabrics was performed using a GT-SONIC-D6 ultrasonicator system (Guangdong GT Ultrasonic Co., Shenzhen, China) operating at a frequency of 40 kHz with an ultrasonic power output of 150 W and heating power of 300 W. The dyebath containing the fabric samples was sonicated under these parametric conditions to enable efficient cavitational effects for enhancement of dye uptake and diffusion into the fibers [19,20].

The mordanted fabrics were dyed by the sonication method using the aqueous dye extract. The dyebath was prepared with a 1:20 liquor ratio and the pH adjusted to 2, 3, or 5 as mentioned earlier. The beaker with the dye bath was placed in an ultrasound sonicator bath and the power was turned on. The temperature was maintained at 70 °C and dyeing was carried out for 30 min. Sonication helps improve dye penetration as well as promoting uniform and even dyeing [19]. The dyed fabrics were removed from the sonicator, rinsed, and dried. A schematic diagram of sonication dyeing is presented in Figure 2. The high-frequency ultrasonic waves disperse dye aggregates and enhance dye diffusion into the fabric structure.

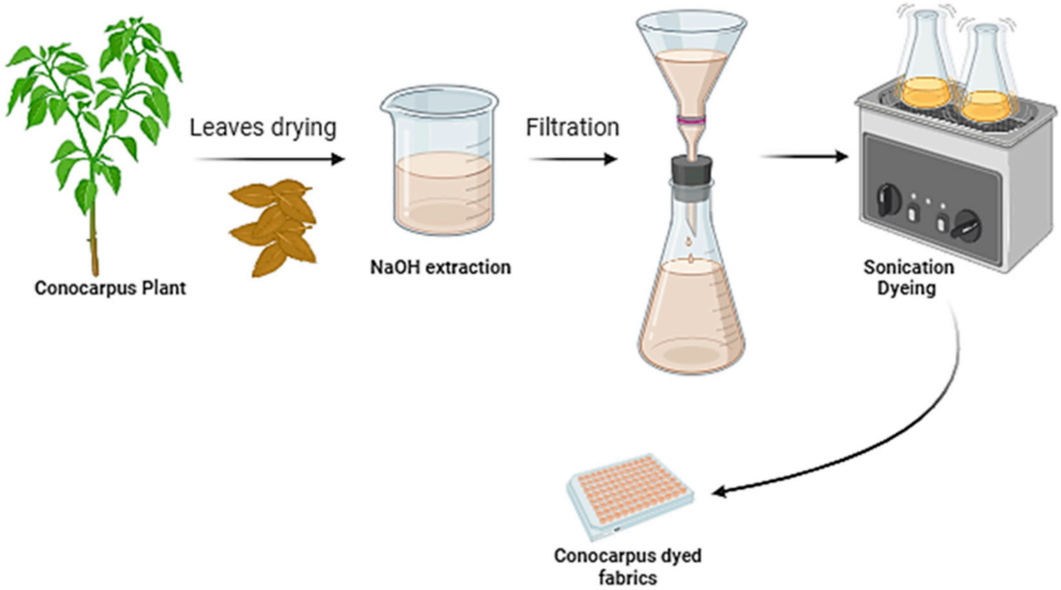

Figure 2. Summaries of extraction from *Conocarpus erectus* leaves and ultrasonic-assisted dyeing of wool and silk.

2.3. Testing Methods

2.3.1. Color Strength Evaluation

The color strength (K/S) values and CIELAB coordinates (L*, a*, b*, C*, h°) of the samples were recorded using a spectrophotometer. Here, L* represents lightness/darkness, a* represents redness/greenness, and b* represents yellowness/blueness values of dyed wool and silk samples. The negative value of a* signifies green and the positive a* describes the red color.

The K/S values were calculated by using the Kubelka–Munk function (Equation (1)):

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

In Equation (1), the reflectance (R), absorption coefficient representation (K), and scattering coefficient (S) of dyed fabric samples were measured at the peak wavelength (λmax) of 350 nm using a spectrophotometer (Color-Eye® 7000A, X-Rite, Grand Rapids, MI, USA. The spectrophotometer was operated with color IQC professional software (v9.0.96.6.) in specular component excluded (SCE) mode to obtain the reflectance data.

2.3.2. Antibacterial Testing

The antibacterial activity of dyed fabrics was tested against Gram-positive *Staphylococcus aureus* bacteria and Gram-negative *Escherichia coli* bacteria using the agar well diffusion method (a qualitative assessment method). Nutrient agar medium plates were inoculated with 100 µL bacterial culture using sterile swabs. Wells were cut into the agar and dyed fabric squares were placed in the wells. The plates were incubated at 37 °C for 24 h and the zone of inhibition around the fabric squares was measured. Clear zones indicated bacterial growth inhibition by the dyed fabrics. In addition, the absence of bacterial colonies below and above dyed fabrics confirms the inhibition activity.

The bacterial inhibition properties of the dyed samples were also determined by quantitative method following the AATCC 100-1999 standard [24]. The same pathogens (*S. aureus* and *E. coli*) were selected as in the qualitative test method. The bacterial inhibition of the dyed samples was calculated by counting the number of bacterial colonies formed in the plates. The number of colonies formed after incubation in the plates of undyed and dyed fabrics was recorded and compared. The bacterial inhibition percentage was calculated by using Equation (2).

$$Reduction\ (\%) = \frac{(A - B)}{A} \times 100 \quad (2)$$

In Equation (2), A is the number of bacterial colonies observed with undyed samples and B is the same with dyed samples.

2.3.3. Colorfastness Testing

The color fastness to washing was determined by the ISO 105-C06 test method [25]. Dyed fabric samples were washed along with multi-fiber fabric for 30 min at 60 °C in a solution containing 5 g/L soap and 2 g/L sodium carbonate. The staining on multifiber strips and color change in dyed fabrics was assessed by a grey scale rating after washing (1–5). According to the grey scale, a rating of 1 signifies poor washing fastness while a rating of 5 signifies excellent washing fastness.

Colorfastness to rubbing was tested by ISO 105-X12 method using a crockmeter [26]. Dyed fabrics were rubbed 10 times with dry and wet white cotton cloth under standard pressure. The color staining on the white cloths was rated on a grey scale (1–5). According to the grey scale, a rating of 1 signifies poor rubbing fastness while a rating of 5 signifies excellent rubbing fastness.

The light fastness of the dyed wool and silk fabrics was evaluated according to ISO 105-B02 color fastness to artificial light standards [27]. The fabrics were exposed to intense xenon arc lamp irradiation for 40 h and the color change was assessed using blue wool scale ratings from 1 to 8. A rating of 8 indicates excellent lightfastness with negligible fading while 1 represents severe fading after light exposure.

2.3.4. UV Protection Testing

The ultraviolet protection factor (UPF) of dyed silk fabrics was measured according to the AS/NZS 4399 standard [28]. A UV-Vis spectrophotometer (model: Shimadzu UV–Vis 1800) was used to record the UV transmission in the range of 200–400 nm. UV transmission through fabric samples was analyzed and UPF was calculated using Equation (3).

$$UPF = \frac{\int_{290}^{400} E_\lambda \times S_\lambda \ \times d_\lambda}{\int_{290}^{400} E_\lambda \times S_\lambda \ \times \tau_\lambda d_\lambda} \quad (3)$$

In Equation (3), E_λ represents the irradiation from sunlight measured in w m^{-2} nm^{-1}, S_λ represents the action of the erythemal spectrum, d_λ is the increase in wavelength, and τ_λ represents the transmission of spectra through the specimen. It is pertinent to mention that higher UPF values indicate greater UV blocking and vice versa.

2.3.5. Mosquito Repellency Testing

The mosquito-repellent property of dyed fabrics was evaluated by a cage test method. Hands covered with untreated and treated fabric gloves were introduced into a cage containing 25 Aedes aegypti mosquitoes for 5 min. The number of mosquitoes landing on each glove was counted and the percent repellency was calculated.

The mosquito landed percentage was calculated from the number of mosquitos introduced and those landed on the respective samples (Equation (4)). However, the percent mosquito repellency was measured using Equation (5).

$$Mosquito\ landed\ (\%) = \frac{No.\ of\ mosquito\ landed\ on\ the\ dyed\ fabric}{No.\ of\ mosquito\ landed\ on\ undyed} \times 100 \quad (4)$$

$$Mosquito\ repellency\ (\%) = 100 - \left(\frac{No.\ of\ mosquito\ landed\ on\ the\ dyed\ fabric}{No.\ of\ mosquito\ landed\ on\ undyed} \times 100 \right) \quad (5)$$

3. Result and Discussion

3.1. Extraction and Dyeing

An aqueous alkaline extraction was employed using sodium hydroxide (NaOH) to aid the dissolution of colorant compounds from the *Conocarpus erectus* leaves. The alkaline medium promotes ionization of phenolic groups, enhancing their solubility in water [29]. The impact of extraction pH on the stability of anthocyanin dyes has been reported [30,31]. Maintaining pH stability above 5 during extraction and dyeing preserves the flavylium cation form of anthocyanins responsible for vibrant colors [31,32].

Aqueous extraction of *Conocarpus erectus* leaves yielded a brown-colored dye solution. The dye uptake and depth of shade increased on the wool and silk fabrics at higher pH (acidic), e.g., anthocyanin stability and absorption at acidic pH [30]. This can be attributed to a greater extent of dye dissolution and increased swelling of fibers facilitating the diffusion of dye molecules into the fabric structure [33]. Wool fabrics showed better dye absorption and deeper hues compared to silk. The amino acids present in the wool fiber structure likely formed strong coordination complexes with the metal mordant and dye compounds.

3.2. Color Strength K/S

The color strength of dyed wool and silk samples was determined in terms of K/S and CIELAB coordinates (L*, a*, b*, C*, h°), which are given in Tables 1 and 2, respectively.

Table 1. K/S values of sonicated dyeing and CIELAB coordinates (L*, a*, b*, C*, h°) of wool dyed with *Conocarpus erectus* dyes.

Wool	K/S	L*	a*	b*	C*	h°	Obtained Shade
Undyed	0.0996	91.49	−0.85	7.32	7.37	96.66	
2 pH	2.4377	58.41	3.97	13.81	14.37	58.41	
3 pH	2.5709	58.66	4.55	15.35	16.01	2.570	
5 pH	1.7833	64.17	3.93	15.31	15.80	75.61	

Table 2. K/S values of sonicated and CIELAB coordinates (L*, a*, b*, C*, h°) of silk dyed with *Conocarpus erectus* dyes.

Silk	K/S	L*	a*	b*	C*	h°	Obtained Shade
Undyed	0.8986	90.34	−0.76	6.22	6.37	95.67	
2 pH	2.3376	56.31	2.99	12.85	13.46	72.87	
3 pH	2.4712	56.57	3.56	14.37	15.03	72.46	
5 pH	1.5683	62.15	1.96	14.34	14.78	74.59	

Likewise, if b* is negative, it is the representation of blue color; on the other hand, the positive b* values indicate yellowness. The L* value ranges from 0 to 100, the lower values indicate the sample is darker than the control sample. The higher K/S value was observed at pH 3 in the case of both wool and silk. The most acidic treatment (pH 3) produced the deepest shade with the highest K/S (2.5709) and lowest lightness (L* = 58.66), along with the highest red-yellow color component (a* = 4.55; b* = 15.35), chroma (C* = 16.01), and lowest hue angle (h° = 73.48). As the pH increased, the depth of shade and chroma progressively decreased, resulting in a lighter and less saturated coloration. At pH 5, the lightest shade among the dyed samples was obtained (K/S = 1.7833; L* = 64.17) with color values closer to the undyed wool. The findings clearly demonstrate the pH-sensitivity of wool dyed under acidic versus neutral conditions, with acidic pH promoting deeper dye uptake and higher chromaticity.

Similarly, the depth shade of silk was maximized (Table 2) at pH 3 dyeing (K/S = 2.4712) along with marginally lower lightness than pH 2 (L* = 56.57). This indicates the most effective dye uptake under slightly acidic versus more acidic or neutral conditions, resulting in the darkest-colored silk with the highest chroma (C* = 15.03).In addition, the acidic dyeing conditions (lower pH) resulted in silk with hue angles shifted towards the red and yellow end of the visible spectrum compared to undyed silk and silk dyed at the higher, neutral pH of 5. The acidic environment enhanced uptake of the red and yellow dyes leading to increased red-yellow coloration in the silk fibers. While pH 3 gave the optimal combination of depth, chroma, and red-yellow hue components, pH 2 and pH 5 dyeing also greatly increased the vibrancy and chromaticity relative to undyed silk. In summary, a slightly acidic pH of 3 promotes superior dye uptake and intense coloration of silk compared to a more acidic or neutral pH.

3.3. Antibacterial Activity

The dyed wool fabrics exhibited antibacterial activity against both *S. aureus* and *E. coli* bacteria, as seen from the zones of inhibition in the agar diffusion tests as shown in Figure 3a,b. Wool fabric dyed at pH 5 showed a clear zone of inhibition against both pathogens (*S. aureus* and *E. coli*). Silk fabrics displayed lower antibacterial effects against both pathogenic microorganisms. However, both fabrics were active in inhibiting bacterial growth, which was validated by the quantitative test (Table 3). It was observed that dyed silk fabric rendered 88.51% and 87.93% reduction in bacterial colonies for *S. aureus* and *E. coli*, respectively, while wool fabric showed 91.22 and 91.98% reduction for *S. aureus* and *E. coli*, respectively.

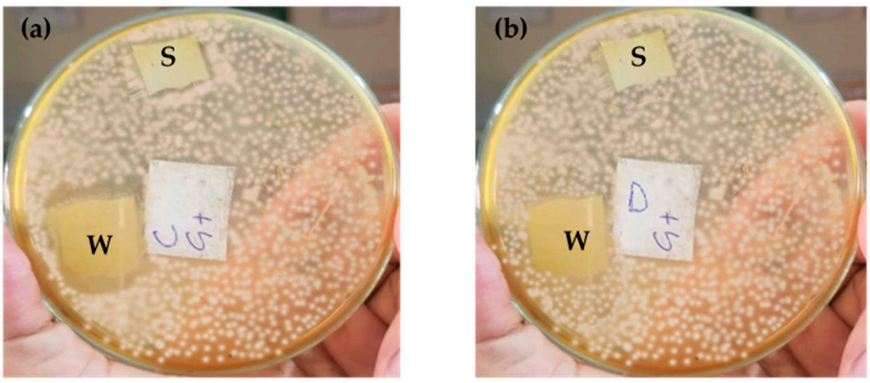

Figure 3. Antibacterial activity of wool and silk dyed at pH 5 (**a**) against *E. coli* (**b**) *S. aureus* using *Conocarpus erectus* extract (where W = wool and S = Silk).

Table 3. Quantitative antibacterial assessment of undyed (silk, wool) and dyed (silk, wool) at pH 5 using AATCC 100-1999 standard.

Sample	No. of Colonies (Cells×000 CFU/mL)		Reduction (%)	
	S. aureus	*E. coli*	*S. aureus*	*E. coli*
Undyed Silk	653	721	-	-
Dyed Silk	75	87	88.51 ± 1.5	87.93 ± 2.1
Undyed Wool	718	723	-	-
Dyed Wool	63	58	91.22 ± 1.8	91.98 ± 2.3

The antimicrobial property can be attributed to the bioactive phytochemicals extracted from the *Conocarpus erectus* leaves and imparted onto the dyed fabrics. Phenolic compounds including flavonoids and tannins are known to have antibacterial effects by disrupting bacterial cell membranes [34]. Previous studies have demonstrated the antibacterial properties of *Conocarpus erectus* extracts attributed to bioactive phytochemicals like flavonoids and tannins [35–38]. These compounds are able to disrupt bacterial cell membranes through interactions with surface proteins and lipids [38]. Our results indicate dyeing confers antibacterial functionality to both silk and wool fabrics, with a higher efficacy seen for wool.

The cationic nature of wool proteins at acidic pH may facilitate electrostatic attractions with negatively charged functional groups of dye molecules [39]. This could enable the binding of dye compounds containing antimicrobial phenolics to cationic sites on wool through charge–charge interactions. Further studies are required to characterize the specific bioactive constituents and their mechanisms of attachment to wool and silk fibers. (Table 3) [40]. Overall, the natural *Conocarpus erectus* dyeing process imparts antibacterial effects to both protein-based fabrics, with an enhanced inhibition activity observed for wool over silk. This demonstrates the potential of sustainable botanical colorants to develop functional textiles preventing microbial growth for medical and hygiene applications.

3.4. Impact of Dye Concentrations on Antibacterial Activity

The antimicrobial efficacy of natural dyes can vary based on the extraction concentrations from plant materials. Higher dye content typically enhances antibacterial effects by increasing the availability of bioactive phytochemicals to disrupt microbial cells [41,42].

In this work, a fixed 1 g/L NaOH extraction adjuvant concentration was employed, which provided sufficient dye uptake for visible coloration. Further optimization of extraction parameters could maximize yields of potent antibacterial fractions.

The dyebath concentration influences the antimicrobial performance of dyed fabrics [43]. Dye concentrations ranging from 2 to 10% o.w.f. were assessed against both Gram-positive and Gram-negative bacteria. Maximum bacterial growth inhibition of 92% for *S. aureus* and 94% for *E. coli* was achieved at 10% dyebath concentration. Antibacterial activity exhibited a positive correlation with increasing dye content due to greater availability of active compounds. The bacterial reduction values are reported along with standard error margins in Table 3 based on triplicate experimental measurements. The low standard error range of ±1.2–2.8 suggests good reliability and repeatability of the antimicrobial testing method.

3.5. Fastness Properties

The dyed wool and silk fabrics exhibited good fastness levels during washing and rubbing, as shown in Tables 4 and 5. The color fastness to washing was rated between 3 and 4 on the grey scale for both changes in shade and staining on the multi-fiber fabric. A rating of 4 indicates negligible change in color. The color fastness to rubbing also ranged from 3 to 4 for dry and wet rubbing with minimal to negligible staining on the white test cloth. Fastness ratings of 3 and above are considered commercially acceptable [44]. The mordant played a key role in improving the fastness by enhancing the binding between the natural dye and fabric [7]. As seen in Table 6, the light fastness of the dyed protein fabrics ranged from moderate to good, with blue wool scale ratings between 5 to 6. Wool dyed at a higher pH of 2, 3, and 5 showed the best light fastness of 5–6. The light fastness of silk was slightly lower compared to wool, with ratings from 4 to 5 under different dyeing conditions. Dyed silk and wool displayed enhanced lightfastness compared to the undyed control fabrics, which faded significantly upon light exposure.

Table 4. Colorfastness to washing wool and silk dyed with *Conocarpus erectus* dyes.

Method	Wool			Silk		
	pH 2	pH 3	pH 5	pH 2	pH 3	pH 5
Shade change	3–4	3–4	3–4	3–4	3–4	3–4
Staining	3–4	3–4	3–4	3–4	3–4	3–4

Table 5. Colorfastness to rubbing wool and silk dyed with *Conocarpus erectus* dyes.

Method	Wool			Silk		
	pH 2	pH 3	pH 5	pH 2	pH 3	pH 5
Wet	3–4	3–4	3–4	3–4	3–4	3–4
Dry	3–4	3–4	3–4	3–4	3–4	3–4

Table 6. Colorfastness to light wool and silk dyed with *Conocarpus erectus* dyes.

Samples	Lightfastness Rating (Silk)	Lightfastness Rating (Wool)
2 pH	4–5	5–6
3 pH	4–5	5–6
5 pH	4–5	5–6

The improved light fastness can be attributed to the binding between fiber amino groups and dye compounds, especially in the presence of the copper mordant. Metal mordants help form coordination complexes leading to superior wash and light fastness. The results indicate the suitability of the sonicated natural dyeing method using *Conocarpus erectus* for producing wool and silk fabrics with good functional properties, in addition to acceptable light fastness.

3.6. UV Protection

The ultraviolet protection factor (UPF) analysis of wool and silk fabrics dyed with *Conocarpus erectus* extract under different pH conditions is presented in Table 7. Undyed silk had a UPF of 14 while undyed wool had a higher UPF of 16, indicating "good" ultraviolet protection (Figure 4). After dyeing, the UPF increased for both fabrics under all pH conditions tested [7]. The highest UPF of 30 (Very Good category) was achieved for wool dyed at pH 3.

Table 7. UPF assessment of dyed and undyed wool and silk samples.

Samples	UPF (Silk)	UPF (Wool)
Undyed	14	16
2 pH	18	23
3 pH	24	30
5 pH	16	27

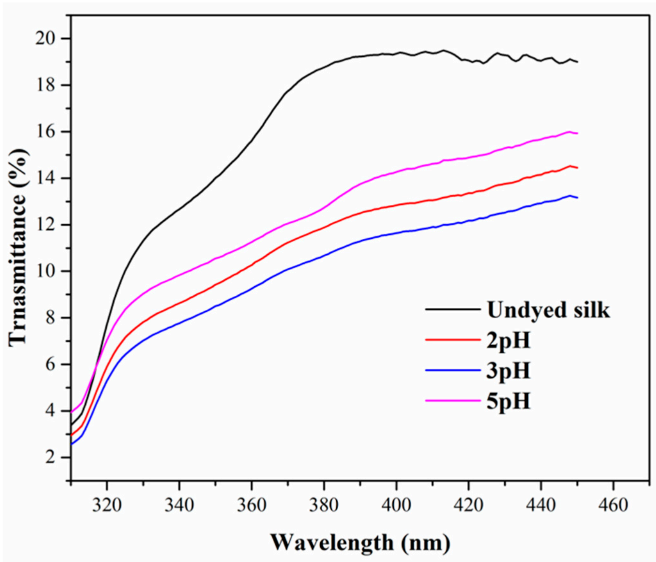

Figure 4. Graphical representation of UPF activity of undyed and dyed silk values.

For silk, the UPF ranged from 18 at pH 2 to 24 at pH 3. Silk showed enhancement of UPF after dyeing, with values ranging from 18 at pH 2 up to 27 at pH 5. The highest UPF of 27 for silk dyed at pH 5 indicates good ultraviolet-blocking ability. Natural colorants like flavonoids and tannins are able to absorb UV radiation thereby improving the ultraviolet protection capacity of textiles [45]. *Conocarpus erectus* leaves contain phenolic compounds which likely imparted UV absorbing characteristics to the dyed wool and silk fabrics in addition to visible coloration. The results indicate the suitability of *Conocarpus erectus* dyes for developing protective clothing and accessories. In addition to dye chemistry, changes in fabric structure during processing can influence UPF. Wet processing often causes fiber swelling and fabric shrinkage, increasing fabric thickness and density [46]. This shrinkage effect reduces porosity and enhances opacity to incident light. While the exact shrinkage was not quantified in this study, some thickening and densification likely occurred for dyed silk and wool. This would contribute to increased ultraviolet reflection and absorption.

Future systematic investigation is required to decouple the individual effects of fiber structural changes from UV-absorbing dye compounds in improving the ultraviolet protection capacity of fabrics.

3.7. Mosquito Repellency

The cage test results shown in Table 8 moderate repellent activity for wool and silk fabrics dyed with *Conocarpus erectus* extracts against *Aedes aegypti* mosquitoes. The cage test experiments for evaluating mosquito repellency of dyed fabrics were performed in triplicate using 25 Aedes aegypti mosquitoes per test. The treated fabric gloves were introduced for a standard 5 min duration for each replicate measurement. The dyed wool and silk samples showed 63–75% protection against mosquito bites based on the percent repellency calculation compared to 31–71% for the undyed fabrics. The repellency was lower than synthetic compounds, but the dye conferred noticeable insect-repelling properties. Plant-derived dyes contain volatile components like terpenoids which are known to have insecticidal effects [47]. Dyeing with botanical colorants like *Conocarpus erectus* offers an alternative eco-friendly approach to developing textiles with mosquito-repelling functionality. While the cage test provides rapid screening, actual wear trials are better indicators of repellent durability over extended durations. Prior studies using plant extracts report effective protection times ranging from 3–6 h after topical application [48]. The current dyeing method produced durable coloration with moderate fastness. Hence, the mosquito repellent effects may potentially persist for several hours of fabric wear, requiring confirmation in future investigations, and further long-term testing will be needed to establish the full duration over which the *Conocarpus*-dyed fabrics can maintain their mosquito repellent activity when exposed to washing, light, and other environmental conditions during usage. But, prior studies on plant-based dyes suggest the Insect-repelling effects persist through multiple wear cycles [49].

Table 8. Mosquito repellency of dyed and undyed wool and silk.

Sample	Total Mosquitos	Landed Mosquitos	Repellency
Undyed Silk	25	18	28%
Dyed Silk	25	8	68%
Undyed Wool	25	19	24%
Dyed Wool	25	16	36%

3.8. SEM Investigations of Silk and Wool and Mechanism of Dye Attachment with Wool

The surface morphology of silk and wool fabrics was examined with scanning electron microscopy (SEM) after dyeing the fabrics with natural dyes extracted from *Conocarpus erectus* leaves. SEM micrographs (Figure 5a,b) revealed an even distribution of dye particles adhered to the surfaces of both silk and wool fibers. Qualitative analysis of the images showed stronger adherence of dye particles to silk fibers compared to wool fibers. The SEM images demonstrated distinct differences in dye particle morphology and surface coverage between silk and wool fibers. On silk, platelet-like dye particles were observed fully coating the fibrils in flaky layers. Wool-dyed areas appeared smoother with more localized dye aggregations. The differential binding and aggregation patterns are likely attributed to inherent variances in the chemical makeup and physical structure of the protein-based fibers.

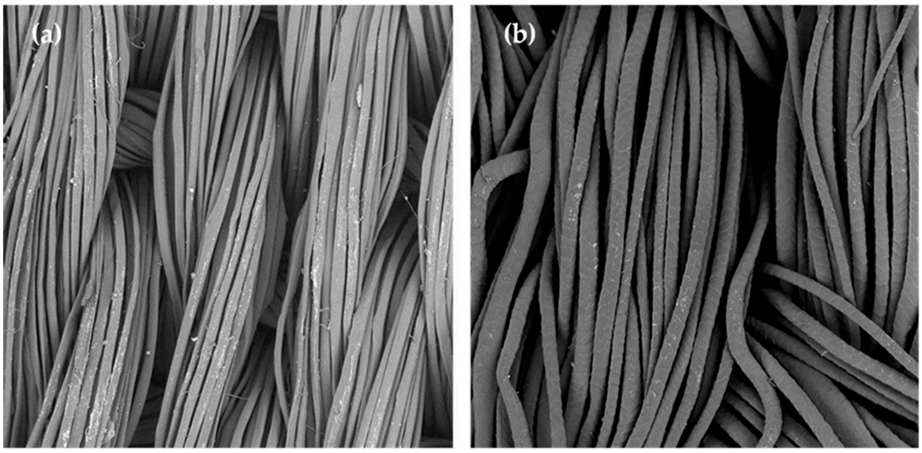

Figure 5. SEM images of silk (**a**) and wool (**b**) after dyeing with ultrasonic assisted from *Conocarpus erectus* dyes at pH 5.

Compared to wool, the natural dye showed a notably higher affinity for silk. Overall, SEM imaging enabled clear visualization of post-dyeing interactions and surface morphologies, serving as an effective materials characterization technique in this study of natural dye binding mechanics with luxury protein fibers.

A mechanism is proposed for dyeing wool with anthocyanin from *Conocarpus erectus* leaves in the presence of Cu^{2+} mordant. The overall process is supported by water H_2O. Due to the strong complex formation between dye and wool fiber, the colorfastness rating is better with mordants such as Al^{3+}, Fe^{2+}, and Cu^{2+}.

3.9. Conclusions

This study demonstrated the extraction of natural dyes from *Conocarpus erectus* leaves and their application to wool and silk fabrics via an ultrasonic-assisted dyeing method. Aqueous alkaline extraction provided a green and sustainable approach to obtaining plant-based dyes. The effects of dyeing process parameters such as pH were examined. Acidic pH was found to be optimal for superior dye uptake and depth of shade on the protein-based fabrics. Sonication at 40 kHz enhanced the dye absorption, diffusion, and uniformity compared to conventional dyeing. In addition to effective coloration, the dyed fabrics displayed functional properties like antibacterial activity against *S. aureus* and *E. coli*, good washing and rubbing fastness, ultraviolet protection, and mosquito repellency. SEM analysis revealed differences in surface morphology and dye aggregation on silk versus wool. The *Conocarpus erectus* dyes displayed a stronger affinity for the silk fibers. Overall, the ultrasonic dyeing method using renewable *Conocarpus erectus* leaf extracts enables sustainable production of colored wool and silk textiles with multiple functionalities. Further characterization of the phytochemical compounds in the dyes can provide directions for enhancement. The results demonstrate the promise of plant-based dyes coupled with ultrasonic techniques for eco-friendly multifunctional textiles.

Author Contributions: Methodology, T.N., K.J. and F.A.; Software, T.N. and K.J.; Validation, T.N., K.J. and F.A.; Formal analysis, T.N. and K.J.; Investigation, T.N. and K.J.; Resources, K.J. and A.K.; Data curation, T.N. and K.J.; Writing—original draft, K.J. and F.A.; Writing—review & editing, K.J., F.A. and A.K.; Supervision, F.A. and M.H.M.; Project administration, M.H.M.; Funding acquisition, A.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: We gratefully acknowledge Muhammad Oneeb at the Department of Parasitology, University of Veterinary and Animal Sciences, Lahore, Pakistan, for his contributions in conducting the cage tests presented in this research.

Conflicts of Interest: The authors declared no competing financial or other interests.

References

1. Křížová, H. *Natural Dyes*; OPS: Kanina, Czechia, 2013; pp. 317–334.
2. Samanta, A.; Agarwal, P. Application of natural dyes on textiles. *Indian J. Fibre Text. Res.* **2009**, *34*, 384–399.
3. Sarkar, A.K. An evaluation of UV protection imparted by cotton fabrics dyed with natural colorants. *BMC Dermatol.* **2004**, *4*, 15. [CrossRef] [PubMed]
4. Kant, R. Textile dyeing industry an environmental hazard. *Nat. Sci.* **2012**, *4*, 22–26. [CrossRef]
5. Che, J.; Yang, X. A recent (2009–2021) perspective on sustainable color and textile coloration using natural plant resources. *Heliyon* **2022**, *8*, e10979. [CrossRef] [PubMed]
6. Bhute, A. Plant based dyes and mordant: A Review. *J. Nat. Prod. Plant Resour.* **2012**, *2*, 649–664.
7. Virendra Kumar, G. Fundamentals of Natural Dyes and Its Application on Textile Substrates. In *Chemistry and Technology of Natural and Synthetic Dyes and Pigments*; Ashis Kumar, S., Nasser, S.A., Hamed Majdooa, A., Eds.; IntechOpen: Rijeka, Croatia, 2019; Chapter 2.
8. Jensen, B.; Evans, R.P.; Tata, G.; Muhlestein, K.; Muhlestein, K.; Jensen, B.V.L.; Pierce, K. Excavations at the Seila Pyramid and Fag el-Gamous Cemetery. In *Chapter 9 They'll Never Be Royals: The "Purple" Textiles of Fag el-Gamous*; Brill: Leiden, The Netherlands, 2019; pp. 207–248.
9. Saxena, S.; Asm, R. *Natural Dyes: Sources, Chemistry, Application and Sustainability Issues*; Springer: Berlin/Heidelberg, Germany, 2014; pp. 37–80.
10. Pizzicato, B.; Pacifico, S.; Cayuela, D.; Mijas, G.; Riba-Moliner, M. Advancements in Sustainable Natural Dyes for Textile Applications: A Review. *Molecules* **2023**, *28*, 5954. [CrossRef]
11. Paramasivam, G.; Manikandan, D.; Subbiah, S.; Durai, M.; Rani, V.; Shunmugiah, M.B.H. Extraction and Applications of Natural dye from the flower of *Tagetes erecta* L. in different Fabrics and Focus on Antimicrobial activity. *Res. J. Pharm. Technol.* **2022**, *15*, 1287–1292. [CrossRef]
12. Kumar, R.; Tripathi, Y. *Natural Dyes from Forest Biomass*; Forest Research Institute: Dehradun, India, 2011; pp. 51–69.
13. Melaku, A.; Demeke, G.; Aschale, M.; Alemayehu, F.; Semegn, G. Extraction and Characterization of Natural Dye Stuff from Spent Coffee Ground and Bio-Mordant from Mango Bark. *J. Nat. Fibers* **2023**, *20*, 2276725. [CrossRef]

14. Ramanjaneyulu, A.; Chaitanya, T.; Joseph, B. *Conocarpus Tree—A Boon or Bane?* Puspa Publishing House: South Dum-Dum, India, 2023.
15. Bashir, M.; Uzair, M.; Ch, B.A. A review of phytochemical and biological studies on *Conocarpus erectus* (Combretaceae). *Pak. J. Pharm. Res.* **2014**, *1*, 1–8. [CrossRef]
16. Naz, R.; Ayub, H.; Nawaz, S.; Islam, Z.U.; Yasmin, T.; Bano, A.; Wakeel, A.; Zia, S.; Roberts, T.H. Antimicrobial activity, toxicity and anti-inflammatory potential of methanolic extracts of four ethnomedicinal plant species from Punjab, Pakistan. *BMC Complement. Altern. Med.* **2017**, *17*, 302. [CrossRef]
17. Lonard, R.I.; Judd, F.W.; DeYoe, H.R.; Stalter, R. Biology of the Mangal Halophyte *Conocarpus erectus* L.: A Review. In *Handbook of Halophytes: From Molecules to Ecosystems towards Biosaline Agriculture*; Grigore, M.-N., Ed.; Springer International Publishing: Cham, Switzerland, 2021; pp. 1819–1831.
18. Hossain, M.K.; Pervez, M.F.; Mia, M.N.H.; Mortuza, A.A.; Rahaman, M.S.; Karim, M.R.; Islam, J.M.M.; Ahmed, F.; Khan, M.A. Effect of dye extracting solvents and sensitization time on photovoltaic performance of natural dye sensitized solar cells. *Results Phys.* **2017**, *7*, 1516–1523. [CrossRef]
19. Shafiq, F.; Siddique, A.; Pervez, M.N.; Hassan, M.M.; Naddeo, V.; Cai, Y.; Hou, A.; Xie, K.; Khan, M.Q.; Kim, I.S. Extraction of Natural Dye from Aerial Parts of Argy Wormwood Based on Optimized Taguchi Approach and Functional Finishing of Cotton Fabric. *Materials* **2021**, *14*, 5850. [CrossRef] [PubMed]
20. Har Bhajan, S.; Bharati, K.A. 4—Mordants and their applications. In *Handbook of Natural Dyes and Pigments*; Har Bhajan, S., Bharati, K.A., Eds.; Woodhead Publishing India: Delhi, India, 2014; pp. 18–28.
21. Lee, K.; Kim, J. Effect of Ultrasound on Disperse Dye Particle Size. *Text. Res. J.* **2001**, *71*, 395–398. [CrossRef]
22. Bhouri, N.; Ltaief, S.; Bhouri, N.; Ben Abdessalem, S. Optimization of a Green Dyeing Process Using Natural Dyes Extracted from Corchorus Olitorius Leaves. *J. Nat. Fibers* **2023**, *20*, 2170946. [CrossRef]
23. Manhita, A.; Ferreira, V.; Vargas, H.; Ribeiro, I.; Candeias, A.; Teixeira, D.; Ferreira, T.; Dias, C. Enlightening the influence of mordant, dyeing technique and photodegradation on the colour hue of textiles dyed with madder—A chromatographic and spectrometric approach. *Microchem. J.* **2011**, *98*, 82–90. [CrossRef]
24. *AATCC-100-1999*; Antibacterial Finishes on Textile Materials. AATCC Committee: Research Triangle Park, NC, USA, 1999.
25. *ISO 105-C06:2010*; Textiles—Tests for Colour Fastness—Part C06: Colour Fastness to Domestic and Commercial Laundering. ISO: Geneva, Switzerland, 2010.
26. *ISO 105-X12:2016*; Textiles—Tests for Colour Fastness—Part X12: Colour Fastness to Rubbing. ISO: Geneva, Switzerland, 2016.
27. *ISO 105-B02:2014*; Textiles—Tests for Colour Fastness—Part B02: Colour Fastness to Artificial Light: Xenon arc Fading Lamp Test. ISO: Geneva, Switzerland, 2014.
28. *AS/NZS 4399*; Sun Protective Clothing—Evaluation and Classification. Standards New Zealand: Wellington, New Zealand, 2017.
29. William, W.A.; Messai, A.M.; Penny, P.G. Phenolic Compounds in Water: Sources, Reactivity, Toxicity and Treatment Methods. In *Phenolic Compounds*; Marcos, S.-H., Mariana, P.-T., Maria del Rosario, G.-M., Eds.; IntechOpen: Rijeka, Croatia, 2017; Chapter 17.
30. Wahyuningsih, S.; Wulandari, L.; Wartono, M.W.; Munawaroh, H.; Ramelan, A.H. The Effect of pH and Color Stability of Anthocyanin on Food Colorant. *IOP Conf. Ser. Mater. Sci. Eng.* **2017**, *193*, 012047. [CrossRef]
31. Cunha, R.; Trigueiro, P.; Cuevas, M.d.M.O.; Medina-Carrasco, S.; Duarte, T.M.; Honório, L.M.d.C.; Damacena, D.H.L.; Fonseca, M.G.; da Silva-Filho, E.C.; Osajima, J.A. The Stability of Anthocyanins and Their Derivatives through Clay Minerals: Revising the Current Literature. *Minerals* **2023**, *13*, 268. [CrossRef]
32. Fossen, T.; Cabrita, L.; Andersen, O.M. Colour and stability of pure anthocyanins influenced by pH including the alkaline region. *Food Chem.* **1998**, *63*, 435–440. [CrossRef]
33. Geetha, B.; Sumathy, J. Extraction of Natural Dyes from Plants. *Int. J. Chem. Pharm. Sci.* **2013**, *1*, 502–509.
34. Ali, N.F.; El-Mohamedy, R.S.R. Eco-friendly and protective natural dye from red prickly pear (Opuntia Lasiacantha Pfeiffer) plant. *J. Saudi Chem. Soc.* **2011**, *15*, 257–261. [CrossRef]
35. Afifi, H.; Marzooqi, H.; Tabbaa, M.; Arran, A. Phytochemicals of Conocarpus spp. As a Natural and Safe Source of Phenolic Compounds and Antioxidants. *Molecules* **2021**, *26*, 1069. [CrossRef] [PubMed]
36. Hussein, N.R.A.; El-Dawy, E.G.A.M. Morpho-anatomical attributes of the Egyptian *Conocarpus erectus* L. (Combretaceae, R.Br.) with its phytochemicals and fungal-endophytes. *Symbiosis* **2023**, 1–19. [CrossRef]
37. Abdulmajid, S.; Al-Azawi, A. Antibacterial Activity of Conocarpus Erectus Leaves Extracts on Some Microorganisms Isolated from Patients with Burn Infection. *Plant Arch.* **2019**, *19*, 583–589.
38. Jasim, N.; Shadhaan, K.; Kadhim, A.; Almohsi, A. Pharmacological and Antimicrobial Properties of Conocarpus Erectus: A Review. *Plant Arch.* **2020**, *20*, 6097–6100.
39. Haroun, A.A.; Mansour, H.F. Effect of cationisation on reactive printing of leather and wool. *Dye. Pigment.* **2007**, *72*, 80–87. [CrossRef]
40. Hassan, M.M. Enhanced insect-resistance, UV protection, and antibacterial and antistatic properties exhibited by wool fabric treated with polyphenols extracted from mango seed kernel and feijoa peel. *RSC Adv.* **2021**, *11*, 1482–1492. [CrossRef]
41. Jubair, N.; Rajagopal, M.; Chinnappan, S.; Abdullah, N.B.; Fatima, A. Review on the Antibacterial Mechanism of Plant-Derived Compounds against Multidrug-Resistant Bacteria (MDR). *Evid.-Based Complement. Altern. Med.* **2021**, *2021*, 3663315. [CrossRef]
42. Hatab, S. Antimicrobial properties and mechanism of action of some plant extracts against food pathogens and spoilage microorganisms. *Front. Microbiol.* **2018**, *9*, 1639.

43. Kumar, D.B.S. Compartive Investigation of Antimicrobial Properties of Medical Fabric Coated with Azadirachta Indica and Ziziphus Jujube. *Int. J. Pharma Sci. Res.* **2017**, *8*, 125–132.
44. Hinsch, E.M.; Robinson, S.C. Mechanical Color Reading of Wood-Staining Fungal Pigment Textile Dyes: An Alternative Method for Determining Colorfastness. *Coatings* **2016**, *6*, 25. [CrossRef]
45. Mongkholrattanasit, R.; Kryštůfek, J.; Wiener, J.; Viková, M. UV protection properties of silk fabric dyed with eucalyptus leaf extract. *J. Text. Inst.* **2011**, *102*, 272–279. [CrossRef]
46. Ivanovska, A.; Dojčinović, B.; Mangovska, B. Studying the influence of common wet processes on the quality of 1 × 1 rib cotton/elastane knitted fabrics. *J. Eng. Fibers Fabr.* **2022**, *17*, 15589250221145522. [CrossRef]
47. Anuar, A.A.; Yusof, N. Methods of imparting mosquito repellent agents and the assessing mosquito repellency on textile. *Fash. Text.* **2016**, *3*, 12. [CrossRef]
48. Baldisserotto, A.; Barbari, R.; Tupini, C.; Buzzi, R.; Durini, E.; Lampronti, I.; Manfredini, S.; Baldini, E.; Vertuani, S. Multifunctional Profiling of Moringa oleifera Leaf Extracts for Topical Application: A Comparative Study of Different Collection Time. *Antioxidants* **2023**, *12*, 411. [CrossRef]
49. Maia, M.F.; Moore, S.J. Plant-based insect repellents: A review of their efficacy, development and testing. *Malar. J.* **2011**, *10*, S11. [CrossRef]