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Neelu Kambo Assistant Professor, Department of Chemistry, UPTTI Kanpur, Kanpur, Uttar Pradesh, India Enhancing the dyeing and functional properties of cotton fabric with the application of natural dyes and nanoparticles

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Abstract

Natural dyes are sustainable, non-hazardous, sustainable and eco-friendly in nature. In addition0to creating subdued shades but also offer the ability to create unique textile substrates with performance attributes like UV protection, deodorizing, antioxidant, antifeedant, and antibacterial qualities. In today's market, creating colorful textile items using natural colorants may increase consumer interest even more. Finding substitute natural degradable dyes has thus emerged as one of the industry's top initiatives in the current environment. Therefore, finding alternative natural degradable dyes has become one of the leading trends in this field in the present scenario.

This study highlights the benefits of natural dyes over synthetic ones, which improves the functional properties of dyed cotton fabric with Punica granatum peel, turmeric, and henna natural dyes with the use of alum as mordant and nanoparticle for environmental benefits.

Keywords: Natural dyes, eco-friendly, nanoparticle, UV protection

Introduction

In general, natural 0 dyes are more environmentally friendly and have superior biodegradability. They are created without the use of chemicals from raw plant or animal components; therefore they are non-toxic, non-allergic, and non-carcinogenic (Pruthi *et al.*, 2008)^[13].

Natural dyes are multi component extracts of unknown concentrations out of which structure of only main component is determined (Singh and Parmar, 1998; Khan, *et al.* 2005) ^[17, 10]. In prehistoric time natural colorants were typically derived from berries, flowers, bark, and roots and these are made without the use of any chemicals. Natural dyes come from various plant parts, leftovers from animals, and certain minerals (Shiva, 2007; Adeel *et al.*, 2019) ^[16, 1]. They come from a variety of sources, including flowers, leaves, insects, bark roots, etc., but they must be extracted and are not easily accessible. They were applied to the fiber without any pretreatment of the dye-material or the textile (Carvalho and Santos, 2016) ^[3].

As synthetic colors became more widely available in the middle of the nineteenth century, the use of natural dyes started to decline. Because of their many benefits, natural dyes are currently a more desirable alternative than synthetic ones. Natural0dyes have several0 benefits, including the ability to be easily extracted into different hues by boiling plants, berries, leaves, bark, or flower heads in water; they are also non-toxic, biodegradable, and visually pleasing, which can lead to the creation of jobs and the use of waste land (Vankar, 2007; Samanta, 2020)^[19, 15].

Even with these benefits, natural dye use is limited to specific regions. These include commercial activities like block printing, boutique work, and artistic forms like Kalmkari. This can be linked to the restrictions placed by these dyes, such as the inability to guarantee shade repeatability, the time-consuming and expensive extraction process, and the variability in the quantity and quality of extraction based on the age and season of the plant, tree, leaves, or fruit, making standardization challenging.

Most of the natural dyes require mordant, which serves as a dye-fixing agent and creates a bond between the dye and the fiber. As a result, it facilitates the production of quicker hues by combining dye and mordant to form an insoluble complex inside the fiber.

Corresponding Author: Neelu Kambo Assistant Professor, Department of Chemistry, UPTTI Kanpur, Kanpur, Uttar Pradesh, India Alum (Aluminum potassium sulfate), chrome (Potassium dichromate), copper (Copper sulfate), iron (ferrous sulfate), and tin (Stannous chloride) are among the common mordants which are used in natural dyeing processes. In the immersion dye process, mordants are added at different times: as a pre-mordant, concurrently with the dyeing process, or after the dyeing process (Samanta and Agarwal, 2009) ^[14]. The metal ions can act as electron acceptors to electron donor to form coordinate bonds with the dye molecules, which are insoluble in water (Thet *et al.*, 2020) ^[20].

Nano particles such as silver, Zink and copper on cotton fabrics improve various characteristics including antimicrobial dyeing, dyeing and UV protection. Dyeing behavior reported when silver nano particles treated fabric dyed with direct dyes (Chattopadhyay and Patel, 2010; Bhandari *et al.*, 2021; Chakrabarty and Jasuja, 2022) ^[4, 2, 5]. The results showed that the application of nano-Ag treatment to cotton, wool, and silk textiles coloured with direct dyes improves the fabric's resistance to microbial assault, light fastness, and washing strength (Perumalraj 2012) ^[12].

Due to stratospheric ozone depletion, researchers0have been focusing more and more on how0to raise the amount of UV radiation (280-400 nm) that reaches the Earth's surface. The effectiveness of a fabric's defence against the dangers of UV radiation is indicated by its UV protection factor (UPF). The level of protection provided by the fabric increases with its UPF value. Fabrics are ranked according to their level of sun protection by the Australian/New Zealand standard, which was the original and is currently the most widely used classification system. Lighter colors tend to reflect solar radiation better than darker ones, which allow energy to enter the cloth through reflection. The greater the shade of a cloth with the same construction and dyestuff, the higher its UV protection factor (UPF). Very light pastel colors only slightly increase fabric UPF; black, navy blues, dark greens, etc., greatly increase it. However, due to unique transmission and absorption properties, different hue dyes can have very different UV protection levels Chakrabarty and Jasuja 2022)^[5]. These results mostly relate to artificial dyes. Below attached table reports (Perumalraj 2012)^[12] on the scant research that examined the UV protection capabilities of natural dyes applied to cotton.

 Table 1: UPF categories with relative transmittance and protection

 0 level

UPF range UPF = UV protection factor	Protection category	UVBE _{ert} transmittance (%)
15-240	Good Protection0	6.7-4.20
25-3	Very0good protection	4.1-2.6
40-5-,50+	Excellent protection	≤2.5

2.1 Materials

- Cotton fabric of simple plane weave.
- Punica granatum peel, Turmeric, Henna herbal (Mehndi) using as natural dyes.
- To enhance colour fastness properties using alum as mordant.
- To study UV Protection Factor of natural dyes using Cu and Zn nano-particles.
- Non-ionic detergent.

Commercially available Mercerised and bleached ready for dye 100 percent cotton0twill fabric was used for dyeing with *Punica granatum* peel, turmeric powder and henna in presence and absence of alum as mordant.

2.2. Method

2.2.1 Pomegranate peel extraction

Pomegranate peels were gathered from nearby vendors selling fresh fruit juice at the neighbourhood market, washed, dried at room temperature (20-25 °C), and crushed into a powder. Pomegranate peel extract (6% mass fraction) was made by extracting the crushed peel in distilled water at a liquor ratio of 1:30 in a water bath at 100 °C for 30 minutes. The mixture was filtered and refrigerated to produce natural colouring.

2.2.2 Turmeric extract

The grocery store in the local Kanpur, Uttar Pradesh market was the source of the pure turmeric powder that was employed in this study as a source of dyes. A distilled water and ground turmeric liquor ratio of 1:30 was extracted in a water bath at 100 °C for 30 minutes to provide a 6% mass fraction of turmeric extract. The mixture was refrigerated and filtered to produce natural colouring.

2.2.3 Henna extract

Fresh henna leaves were collected from the campus of UPTTI, cleaned, and then allowed to dry at room temperature (20-25 °C) before being ground into a powder. To create henna extract with a mass fraction of 6%, ground henna was extracted in distilled water at a liquor ratio of 1:30 in a water bath at 100 °C for 30 minutes. The mixture was cooled and filtered to create natural coloring.

2.2.4 Dyeing of cotton with *Punica granatum* peel, Turmeric, Henna without any chemical

All dyeing was done in a lab dyeing machine using 6% dye on the sample weight with liquor to material ratio of 20:1 at 50 °C for 10 minutes. After 30 minutes of gradual temperature increase, the dyeing process was kept at a boil for an additional 45 minutes. Samples were cleaned for thirty minutes under cold running water.

2.2.5 Dyeing of cotton with *Punica granatum* **peel, Turmeric, Henna using alum as a Mordant:** All dyeing was done in a lab dyeing machine using 6.0% dye on the sample weight, with liquor to material ratio of 20:1. Three steps are involved in the mordanting procedure.

- 1. **Premordanting:** Firstly, materials were treated with 8% alum weight at 80 °C for 30 minutes, and then rinsed under cold running water. Following that, dyeing is done.
- **2. Simultaneous mordanting:** 8% alum was applied during the dyeing process.
- **3. Postmordanting:** in this procedure, dyeing was done before mordanting.

The sample was treated for 10 minutes at 50 °C. After 30 minutes of gradual temperature increase, the dyeing process was kept at a boil for an additional 45 minutes. Samples were cleaned for 30 minutes under cold running water.

2.2.6 Dyeing of cotton with *Punica granatum* peel, Turmeric, Henna using nanoparticles

2.2.6a Nano Cu Treatment on the Cotton Fabric

- Using the exhaust process, the produced nano Cu dispersion was applied to cotton fabric. 1 ml of Cu dispersion in 100 ml of water to generate a 1% solution by using a material to liquor ratio of 1:50, weigh 1% of the cloth at 40 °C. The treatedOfabric samples wereOcompletely cleaned and then the temperature was raised to 80 °C during a 30-minute period after one hour.
- Every dyeing process was done in a lab dyeing machine with a liquor to material ratio of 20:1, using 6% dye based on the sample weight. The sample underwent a 10-minute treatment at 50 °C.
- After 30 minutes of gradual temperature increase, the dyeing process was kept at a boil for an additional 45 minutes. Samples were cleaned for 30 minutes under cold running water.

2.2.6b Nano Zn Treatment on the Cotton Fabric

- Using 6.0% dye on the sample weight, all dyeing was done in a lab dyeing machine with liquor to material ratio of 20:1. For ten minutes, the sample was treated at 50°C. After 30 minutes of gradual temperature increase, the dyeing process was kept at a boil for an additional 45 minutes. Samples were cleaned under cold running water for 30 mins.
- Every dyeing process was done in a lab dyeing machine with a liquor to material ratio of 20:1, using 6% dye based on the sample weight. The sample underwent a 10-minute treatment at 50 °C. After 30 minutes of gradual temperature increase, the dyeing process was kept at a boil for an additional 45 minutes. Following sample washed under cold running water.

2.2.7 Evaluation of Dyed Samples

The effect of nano Cu and Zn treatment on the dyeability of natural dyes on cotton fabric in terms of K/S was measured on computer colour matching system (Spectra Scan 5100 (RT)) spectrophotometer inter-phased.

2.2.7a Fastness Testing: Following a 24-hour period of partial exposure to a xenon arc lamp, the light fastness of the dyed samples was assessed using a fad-o-meter, and the color change was rated. Using a lounder-o-meter (Digi. wash, Paramount Scientific Instruments, India), the samples' wash fastness was tested in accordance with ISO-2 test procedures. The samples were assessed based on how much their color changed.

3. Results and Discussion

3.1 Dyeing behaviour of cotton fabric using alum as mordant: Colour strength in terms of K/S value of dyed cotton fabrics for untreated, mordanted with alum, and treated with nanoparticles are shown in table 1 and also in Fig. 1. From the table 2 it is observed that K/S values of dyed fabrics without mordant are 8.8, 3.32, 3.28 for Punica granatum peel, turmeric, henna colorants respectively. It indicates that Punica granatum peel colourants gives highest K/S value of cotton fabric followed by turmeric and henna without any mordanting/treatment. It is further observed that the K/S value improves significantly for dyed cotton fabric after post mordanting using alum as a mordant in Punica granatum peel. However, cottOnfabric dyedOwith turmeric dye shows higher K/S value in simultaneous mordanting method usingOalum as a mordant. The cotton fabric dyed with henna colorants gives higher K/S value using alum mordant than without mordanting.



Fig 1: K/S value of cotton fabric dyed using different natural colorants

Table 2:	K/S	value	for	different	colorants	for	different	mordanting	process
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Dyes name	K/S Value for Pre mordanting	K/S Value for Simultaneous mordanting	K/S Value for Post mordanting	K/S Value for without any chemical
Punica granatum peel	19.026	8.715	13.31	8.80
Turmeric	9.768	15.685	5.902	3.321
Henna	6.987	6.675	3.996	3.287

3.2 Dyeing behaviour of cotton fabric using Cu and Zn nanoparticles: Three natural colorants were used to dye the cotton fabric0samples treated with Cu and Zn nanoparticles,

and the results were compared to the untreated samples. The K/S values of cotton dyed samples using different colorants pre-treated with nano particles samples0are shown in table 3

and also in Fig 2. It is observed that pre-treated fabric samples with Cu and Zn nanoparticle and subsequently dyed with natural colourants have higher K/S value than the corresponding untreated dyed cotton fabrics. Since the presence of nano metal particles increases the dye's affinity for cotton fibers, they operate as a mordant, as seen by the higher K/S values of the coloured samples treated with nanotechnology. Tiny particles serve as filler or cross-

linking agents by getting in between the molecules of the cotton polymer. This causes the cotton fibers' propensity for dye to grow. The polarity that the induction of polarity in the metal particles produced in the negatively charged dye anions likely drew them to the fiber, improving the binding between the dye and the fiber ((Chattopadhyay and Patel 2010)^[4].

Table 3: K/S value for different colorants for Cu/Zn nanoparticles and without chemical

Dyes name	K/S value of treated with Cu nanoparticle	K/S value of treated with Zn nanoparticle	K/S value of untreated with any chemical
Punica granatum Peel	14.389	12.902	8.800
Turmeric	6.527	4.442	3.321
Henna	3.294	3.760	3.287



Fig 2: K/S value of cotton fabric dyed using different natural colourantsin presence of alum as mordant and with Cu/Zn nanoparticles

3.3 Fastness properties of dyed fabrics

3.3.1 Light fastness

The colour fastness properties of nano particle treated and alum mordanted cotton fabric are shown in table 4 and also Fig 3. It shows that dyed sample using *Punica granatum* peel extracted dye after mordanting with alum and treated with Cu/Zn nanoparticle has light fastness rating 6 and 7 respectively. It is clearly indicating that Cu/Zn nanoparticle treated fabrics dyed with *Punica granatum* peel dye has better light fastness than mordanting with alum. Similarly cotton fabric dyed with henna after mordanting with alum and treated with Cu/Zn nanoparticles has light fastness rating 4-5 and 6 respectively. In case of cotton fabric dyed with turmeric after mordanting with alum and pre-treatment with Cu/Zn nanoparticles have shown light fastness rating 3-4 and 4-5 respectively. From the above results it clearly depicts that cotton fabric dyed with *Punica granatum* peel has highest light fastness followed by henna and turmeric dyed cotton fabrics. As discussed earlier that the K/S value after mordanting or pre-treatment of Zn/Cu nanoparticles improves significantly due to cross linking of dye molecules with fibre. The enhanced color fastness capabilities are another indication of the improved dye-fiber interaction. When utilizing 2 g/l non-ionic detergent to wash out materials that had been treated or left untreated and dyed, the Cu-Zn nano treated and dyed sample remained nearly untouched by the process. Therefore, the copper nano pretreatment enhanced both the color strength and the fastness, which addresses a significant issue with most dyes' color fastness. However dyeing with henna using Cu/Zn nanoparticles does not show any change in K/S value of dyed cotton samples (Gulrajani 2001) [8] reported that colour fastness properties of henna powder moderate to good, similar results are also obtained (Mittal et al. 2015)^[11].

Fable 4:	light	fastness	of cotton	dyed	fabrics
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Dyes Names	Chemical Name	Method	Rating
Punica granatum		Pre mordanting	
	Alum	Simultaneous mordanting	6
		Post mordanting	6
	Cu nano particle		7
	Zn nano particle		7
		Pre mordanting	3-4
Turmeric	Alum	Simultaneous mordanting	3-4
		Post mordanting	3-4

	Cu nano particle		4-5
	Zn nano particle		4-5
		Pre mordanting	4-5
	Alum	Simultaneous mordanting	4-5
Henna		Post mordanting	5
	Cu nano particle		6
	Zn nano particle		6



Fig 3: Light fastness of cotton fabric dyed using different natural colourants in presence of alum as mordant and with Cu/Zn nanoparticles

3.3.2 Washing fastness

The results of washing fastness of different cotton dyed fabrics are shown in table 5 and also in Fig. 3 among the different dyes used for cotton dyeing, the cotton fabric dyed with henna has shown very good washing fastness for mordanted with alum as well as pre-treated Cu/Zn nanoparticles. Dyed0cotton fabric using *Punica granatum* peel after mordanting with alum and pre-treatment with Cu/Zn nanoparticles has shown good to very good washing fastness properties. However, cotton fabric0dyed with

turmericOnatural colourants has shown fair washing fastness for alum mordanted and good for pre-treated with Cu/Zn nanoparticles. From the above discussion it could be concluded that henna and *Punica granatum* peel natural dye have superior washing fastness properties than turmeric natural dye using alum mordant as well as Cu/Zn nanoprticle as pre-treatment. Turmeric and *Punica granatum* peel colorants act as direct dyes (Iqbal *et al.* 2008) ^[9].

Dyes Names	Chemical Name	me Method		Rating CS
		Pre mordanting	3	2.5
	Alum	Simultaneous mordanting	3.5	3
Punica granatum	Γ	Post mordanting	3.5	3
	Cu nano particle		3.5	3
	Zn nano particle		3.5	3
		Pre mordanting	2	4
	Alum	Simultaneous mordanting	2	4
Turmeric		Post mordanting	2	4
	Cu nano particle		3	4
	Zn nano particle		3	4
		Pre mordanting	4	4
Henna	Alum	Simultaneous mordanting	3	4
	Γ	Post mordanting	4	4
	Cu nano particle		4	4
	Zn nano particle		4	4

Fable 5: washing0fastness of cotton dye	d0fabrics
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Fig 4: Washing fastness of cotton fabric dyed using different natural colourants in presence of alum asmordant and with Cu/Zn nanoparticles

3.3.3 Rubbing fastness

The rubbing fastness of cotton dyed fabrics using with *Punica granatum* peel, turmeric, henna colourants using alum as a mordant as well as Zn/Cu nanoparticles shows, Table 6 and also Fig. 5, good to very good rating in both dry

and wet conditions. It could be concluded that dyeing with natural colour from *Punica granatum* peel, turmeric and henna using alum mordant and Cu/Zn nanoparticles produced colour on cotton fabric resists to rubbing action in dry and wet states.

Dyes Names	Chemical Name	Method	Rating in dry condition	Rating in wet condition
		Pre mordanting	4	3-4
	Alum	Simultaneous mordanting	4	3-4
Punica granatum peel		Post mordanting	4	3-4
	Cu nano particle		4-5	4
	Zn nano particle		4-5	4
Turmeric		Pre mordanting	4	3-4
	Alum	Simultaneous mordanting	4	3-4
		Post mordanting	4	3-4
	Cu nano particle		4-5	4
	Zn nano particle		4-5	4
		Pre mordanting	4-5	4
Henna	Alum	Simultaneous mordanting	4-5	4
		Post mordanting	4-5	4
	Cu nano particle		4-5	4
	Zn nano particle		4-5	4



Fig 5: Rubbing fastness of cotton fabric dyed using different natural colourants in presence of alum as mordant and with Cu/Zn nanoparticles

3.3.4 UV protection properties of Natural dyes

The reported UVA and UVB values of different natural dyed cotton fabrics are shown in Table 7 It is observed that UVA and UVB (%) transmittance (Table 8 and Fig 6) of henna and turmeric natural colourant are 18 and 22% and 16 and 11.5% without treatment. A significant reduction is observed in UVA and UVB values of dyed fabrics after mordanting with alum and treatment with Zn/cu nanoparticles. The UPF values of dyed fabrics with henna and turmeric are found in less than 40, which provide moderate to good protection from ultra violet radiation. The fabrics dyed with *Punica granatum* peel colourant without mordant gives 6.17% and 4.92% UVA and UVB transmittance values gives good protection against ultra

violet radiation. When the fabric is dyed with *Punica* granatum peel colourant using alum mordant significantly improves the UVA and UVB transmittance value below 4% and UPF (Fig 7) increased to more than 60. The UPF is found highest 233 for pre- mordanting followed by post and simultaneous mordanting dyeing process. The dyeing with *Punica granatum* peel colourant has qualified AS/NZS4399 standard for UV protection. The UV protection for *Punica granatum* peel is achieved at excellent level. The dyeing of cotton fabric with *Punica granatum* peel after treatment with Cu/Zn nano particles also shows excellent UPF and qualified S/NZS4399 standard for UV protection (Grifoni *et al.* 2009, Crews *et al.* 1999)^[7, 6].

Table 7: Standard Ultra-Violet Transmission Analysis (Grifoni et al. 2009)^[7].

UPF range UPF = ultraviolet protection factor	Protection category	UVBE _{eryt} transmittance (%)
15-24	Good protection	6.7-4.2
25-	Very good protection	4.1-2.6
40-50,50+	Excellent protection	≤2.5

Dyes Names	Chemical Name	Method	UVA (%)	UVB (%)	UPF
Punica granatum	Alum	Pre mordanting	1.20	1.09	233.3
		Simultaneous mordanting	3.85	2.77	64.1
		Post mordanting	2.95	2.42	73.3
	Cu nano particle		2.55	1.95	87.8
	Zn nano particle		3.07	2.56	68.7
	Without treatment		6.13	4.92	46.0
Turmeric	Alum	Pre mordanting	7.88	9.62	24.3
		Simultaneous mordanting	8.47	11.76	21.7
		Post mordanting	10.79	13.03	19.8
	Cu nano particle		9.80	11.39	26.6
	Zn nano particle		11.84	13.79	18.8
	Without Treatment		17.79	22.07	12.0
Henna	Alum	Pre mordanting	10.13	9.49	24.2
		Simultaneous mordanting	7.53	6.34	35.9
		Post mordanting	16.60	17.83	14.6
	Cu nano particle		10.85	10.10	24.5
	Zn nano particle		15.95	15.84	17.1
	Without Treatment		15.99	11.46	14.9

Table 8: Ultra-	 Violet Transmission 	n Analysis
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Fig 6: Ultra-Violet Transmission Analysis (UVA and UVB %) of cotton fabric dyed using different natural colourants in presence of alum as mordant and with Cu/Zn nanoparticles



Fig 7: Ultra-Violet Transmission Analysis (UPF) of cotton fabric dyed using different natural colourants in presence of alum as mordant and with Cu/Zn nanoparticles

3.4 Discussion

The study emphasizes the advantages of natural dyes over synthetic ones, including their eco-friendliness and nontoxicity as well as their biodegradability. Natural dyes drew researchers in traditional and varied applications to develop efficient eco-friendly and cleaner process technologies as awareness of eco-friendly materials from sustainable resources increased. This discussion is on the potential for integrating natural dyes with innovative techniques like nanoparticle treatment to create fabrics with improved functionality and environmental benefits. The results point to a possible path for environmentally friendly textile dyeing techniques.

The study discovered that, when dyed with pomegranate peel using alum as a mordant, pomegranate peel offers the strongest color (K/S value), followed by henna and turmeric. K/S values were further enhanced by cu/Zn nanoparticle treatment.

Fastness Properties also improves the use of mordants and nanoparticles with the dyed fabrics. The study also looked into the dyed fabrics' ability to block UV rays. *Punica granatum* peel-dyed fabrics treated withOalum and nanoparticles demonstrated superior UV protection.

4. Conclusion

This study highlights the benefits of using natural dyes over synthetic dyes, focusing on their eco-friendliness, nontoxicity, and biodegradability. The research demonstrates that natural dyes, particularly when used in conjunction with mordants like alum and nanoparticle treatments, can significantly enhance the dyeing performance of cotton fabrics.

4.1 Key findings include

- 1. Color Strength (K/S Value): The Punica granatum peel dye produced the highest color strength, followed by henna and turmeric. The application of alum as a mordant and the use of Cu and Zn nanoparticles further enhanced the K/S values, indicating improved dye affinity and color strength.
- **2. UV Protection:** Fabrics dyed with Punica granatum peel and treated with alum and nanoparticles showed superior UV protection, suggesting potential for creating textiles with added functional benefits.

- **3. Fastness Properties:** The study found that the use of mordants and nanoparticles improved the fastness properties of the dyed fabrics. Specifically, henna and Punica granatum peel dyes exhibited superior washing fastness compared to turmeric.
- **4. Environmental Impact:** The integration of natural dyes with innovative techniques like nanoparticle treatment offers a promising pathway for developing environmentally friendly textile dyeing processes.

These findings suggest that combining natural dyes with mordants and nanotechnology can create high-performance, eco-friendly textiles suitable for various applications. This approach not only leverages the inherent benefits of natural dyes but also enhances their functional properties, contributing to more sustainable and environmentally conscious textile production.

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