Mordant-Free Dyeing of Organic Cotton Using Tea Extracts: Waste-to-Color

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Abstract. The valorization of green tea waste as a sustainable natural dye for organic cotton fabrics offers a promising alternative to synthetic dyes, mitigating environmental and health risks. We developed a mordant-free, ultrasonic-assisted dyeing protocol that maximizes dye uptake and fastness while minimizing energy consumption. Systematic optimization revealed 55 °C as the ideal dyeing temperature, achieving superior color strength (K/S = 1.445) and excellent wash and rub fastness without compromising fiber integrity. Mechanistic insights from physicochemical analyses demonstrated enhanced polyphenol–cellulose interactions facilitated by ultrasonic cavitation. This eco-friendly approach promotes circular bioresource utilization and advances green textile coloration.

Keywords: Mordant-free dyeing, Organic cotton, Waste-to-Color, Green tea dyes, Ultrasonic-assisted dyeing.

1 Introduction

The textile industry remains one of the largest consumers of synthetic dyes, particularly for cotton dyeing, owing to their wide color range, excellent fastness properties, and cost-effective production [1]. However, the widespread use of synthetic dyes has raised serious environmental and health concerns [2]. Many of these dyes are composed of complex aromatic structures that are highly resistant to degradation, leading to persistence in aquatic systems [3]. Even at concentrations below one ppm, synthetic dyes can impart visible coloration to water, obstructing light penetration, impairing photosynthesis, and disrupting aquatic ecosystems. Additionally, certain synthetic dyes have been associated with toxic, allergenic, and carcinogenic effects, raising public and regulatory concern [4]. In response to these challenges, interest in natural and alternative dyes has resurged, driven by global efforts toward sustainable and environmentally responsible textile production [5]. Natural dyes are typically biodegradable, less toxic, and derived from renewable sources, making them attractive alternatives to their synthetic counterparts [6]. A wide array of plant parts (including bark, roots, flowers, leaves, and seeds) has been successfully explored as dye sources for cotton fabrics. For example, our previous study demonstrated that dye extracts from *Macadamia integrifolia* showed promising results for natural cotton dyeing [7].

Despite this progress, the utilization of agricultural waste as a source of textile dyes remains underexplored [8]. Agro-industrial residues such as banana peels, pomegranate rinds, and eggplant skins contain significant quantities of bioactive compounds but are often discarded [9]. Converting such waste into value-added products not only aligns with circular economy principles but also mitigates environmental burden. In this context, green tea (*Camellia sinensis*) waste (generated in large volumes during beverage processing) emerges as a viable, untapped source of natural dye [10]. Green tea leaves are rich in catechins, polyphenolic compounds with intrinsic chromophoric properties. The major catechins include epigallocatechin gallate, epicatechin gallate, epigallocatechin, and epicatechin (**Figure 1**b), which possess a high affinity for cellulose fibers through hydrogen bonding and van der Waals interactions [11]. Previous studies have reported the use of tea-based dyes in conjunction with metallic mordants such as iron, aluminum, copper, and zinc to enhance shade and fastness [12]. However, the dependence on mordants presents sustainability challenges due to the potential toxicity and environmental accumulation of heavy metals.

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To date, little is known about the direct application of green tea waste as a natural dye source for cotton without mordants. This study seeks to bridge this gap by valorizing spent green tea leaves as a dye precursor for organic cotton fabrics via a sustainable, ultrasonic-assisted dyeing method. The objective is to develop a mordant-free dyeing protocol that maximizes color uptake, fastness, and environmental compatibility. Temperature, a key dyeing parameter, was systematically optimized. The dye–fiber interaction mechanisms were further elucidated through surface morphology (SEM), structural (XRD), and colorimetric (CIELab*, K/S) analyses. This approach not only proposes a low-cost and eco-friendly alternative for textile coloration but also contributes to green waste management in the agro-industrial sector.

2 Experimental

2.1 Materials

Bleached 100% knitted organic cotton fabric (OCF, 130 g/m²) was provided by Changzhou Jiaqi Textiles (Jiangsu, China). Green tea leaves were obtained from Hengli Tea Co., Ltd. (Zhejiang, China). Nonionic detergent, absolute ethanol, and tannic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used without further purification, and deionized water was employed throughout the wet processes.

2.2 Tea dying of OCF

Preparation of dye powder: Green tea leaves were washed at 65 °C for 5 min, sun-dried, and manually cleared of impurities. The dried waste leaves were ground into a fine powder using a 1600 W, 50 Hz high-speed grinder (COSUAI, China). The powder was vacuum-packed and stored at room temperature to maintain dryness for subsequent use.
Extraction of dyes: Natural dye was extracted from waste green tea leaves using a solvent extraction method. Finely ground leaf powder (26.66 g) was mixed with 400 mL of solvent [60% ethanol, 40% deionized water; material-to-liquid ratio (M: L) of 1:15] and stirred at 2000 rpm for 30 min. The mixture was then heated at 55 °C for 45 min in a digital water bath (HH-S2, 800 W) while covered with aluminum foil to minimize evaporation. After extraction, the solution was filtered using filter paper, and the pH was maintained at 5–6. All procedures were carried out under controlled conditions to maximize dye solubility and preserve extract integrity.
Pretreatment of OCF: Pre-scoured and bleached OCF was desized in a 3.5 g/L non-ionic detergent solution (M: L = 1:20) at 95 °C for 1 h using a temperature-controlled water bath. The fabric was then rinsed thoroughly with deionized water and air-dried at room temperature. Subsequently, OCF was treated with 4% tannic acid solution (M: L of 1:20) for 5 h at room temperature, rinsed, squeezed, and air-dried under ambient conditions. The entire process of dyeing is schematically presented in **Figure 1:a**.
OCF dyeing process: Pretreated OCF was dyed in an ultrasonic bath containing natural dye at an M: L of 1:20 at varying temperatures (45 °C, 55 °C, 65 °C, and 75 °C) for 60 min (labeled as dyed OCF/Temp., e.g., OCF/45). Ultrasonic treatment enhanced dye penetration and uniformity, enabling efficient uptake in a shorter time. Dyed samples were rinsed with deionized water and washed (M: L of 60:1) in 3.5 g/L non-ionic detergent at 50 °C for 10 min, then air-dried at room temperature to ensure color uniformity and good fastness.

2.3 Optimization and Characterizations

Optimization of OCF dyeing was investigated at four temperatures (45–75 °C) over 60 minutes. Efficiency was evaluated by color strength (K/S), uniformity, and dye exhaustion. The results indicated that 55 °C offered an optimal balance between dye uptake and energy consumption, reducing waste and environmental impact, whereas 75 °C led to potential dye degradation and inefficiency. Dyeing efficiency [$m_1 / (m_1 - m_2) \times 100\%$] was calculated using the standard formula, where m_1 represents the dye weight used and m_2 the residual dye weight.

Surface morphology of OCF was examined via SEM at 5.0 kV using a HITACHI TM4000. The crystal structure was analyzed by XRD (Rigaku Ultima III). Dyed fabric color properties were assessed through color strength (K/S), CIELab* coordinates, and colorfastness (washing and rubbing). Detailed characterization and performance analyses followed the protocols from our previous study [13].

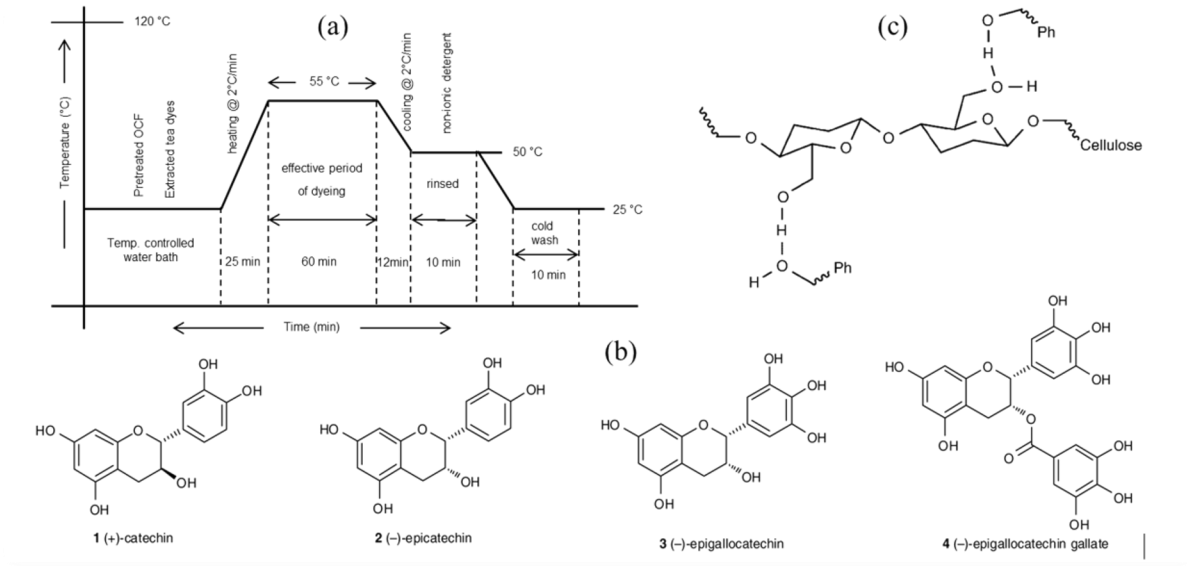

Figure 1. (a) Process curve of OCF tea dying, (b) Tea phytochemicals: structures of (+)-catechin and (−)-epigallocatechin gallate, (c) Interaction between cellulose of OCF and phenolic compound in tea (Figures b and c were reproduced with permission [11], Copyright, Wiley 2018).

3 Results and Discussion

In the temperature-dependent tea dying of OCF, the K/S values were 0.908, 1.445, 1.304, and 0.940, respectively (**Figure 2**a), with 55°C yielding the highest dye uptake. This optimum is attributed to enhanced fiber swelling and molecular mobility, which improve dye diffusion and binding [14]. At lower temperatures (45°C), limited kinetic energy reduces dye penetration, while at higher temperatures (65–75°C), excessive thermal energy may disrupt hydrogen bonding or cause partial degradation of polyphenolic dyes, lowering their affinity for cellulose [15]. Colorimetric analysis (**Table 1**) revealed that undyed OCF samples exhibited high lightness ($L^* \approx 88–89$), slight green tones ($a^* < 0$), and mild yellow hues ($b^* \approx 2.9–3.0$), with minimal absorption at 400 nm ($K/S \approx 0.106–0.124$). Dyeing markedly reduced L* (darkening), while increasing a* and b* values, indicating a shift toward red-yellow tones. This calorimetric is also observed in the physical photographs of samples (**Figure 2**d). Moreover, peak color strength was observed at 55 °C ($K/S = 1.445$, $a^* = 5.358$, and $b^* = 13.482$), attributed to optimal fiber swelling and molecular mobility facilitating polyphenol–cellulose interactions. At 75 °C, color strength declined ($K/S = 0.94$), likely due to thermal degradation of tea polyphenols and disrupted hydrogen bonding, limiting dye uptake efficiency [12]. Tea-dyed OCF showed excellent wash fastness (color change = 5) and strong staining resistance across multifiber strips (acetate/nylon = 4–5, cotton/acrylic/wool = 5, and polyester = 4) (**Table 2**). The performance is attributed to strong interactions (such as hydrogen bonding and potential esterification) between polyphenolic dye groups (–OH, –COOH) and cellulose [16]. Ultrasonic dyeing further enhanced dye diffusion and fixation. While dry rub fastness was high (4–5), slightly reduced wet rub fastness (4) indicates minor dye migration due to water-soluble fractions.

Table 1. Color measurements of OCF (at an illuminant of D65/10° and K/S values at 400 nm wavelength)

OCF samples	L^*	a^*	b^*	K/S
Undyed OCF/45	88.221	-0.07	2.928	0.124
Undyed OCF/55	89.228	-0.078	2.956	0.106
Undyed OCF/65	88.701	-0.066	3.02	0.117
Undyed OCF/75	89.19	-0.16	2.925	0.107
Dyed OCF/45	70.703	4.631	9.734	0.908
Dyed OCF/55	67.35	5.358	13.482	1.445
Dyed OCF/65	68.307	4.784	11.482	1.304
Dyed OCF/75	71.799	4.346	9.355	0.94

Table 2. Color fastness properties of tea dyed OCF

CFR (dry)	CFR (wet)	Color Change	Acetate/Nylon†	Cotton/Acrylic/Wool†	Polyester†
4-5	4	5	4-5	5	4

CFR- colorfastness to rubbing, †Color fastness to wash (color staining on different fibers).

SEM analysis (**Figure 2**c) revealed significant morphological differences between undyed and green tea–dyed organic cotton fibers. Ultrasonic treatment induced surface swelling and roughness, facilitating enhanced pigment adherence [17]. Dye fixation occurred through two complementary mechanisms [13]: physical immobilization of larger polyphenolic aggregates within the fiber network, and molecular adsorption of smaller molecules into cellulose pores. Ultrasonication increased fiber porosity and molecular mobility, promoting deeper penetration and stronger hydrogen bonding between dye phytochemicals and cellulose hydroxyl groups, thus improving dye uptake and fixation [14], [17]. XRD analysis (**Figure 2b**) revealed a dominant peak at $2\theta \approx 22°$, characteristic of native cellulose I. Post-dyeing, peak intensity decreased and broadening occurred, indicating reduced crystallinity and increased amorphous regions. This structural disruption is attributed to ultrasonic cavitation, which transiently breaks hydrogen bonds, enhancing dye penetration. Crucially, the cellulose's crystalline core remains intact, enabling improved dye uptake without compromising fiber integrity, underscoring the sustainable potential of mordant-free ultrasonic dyeing.

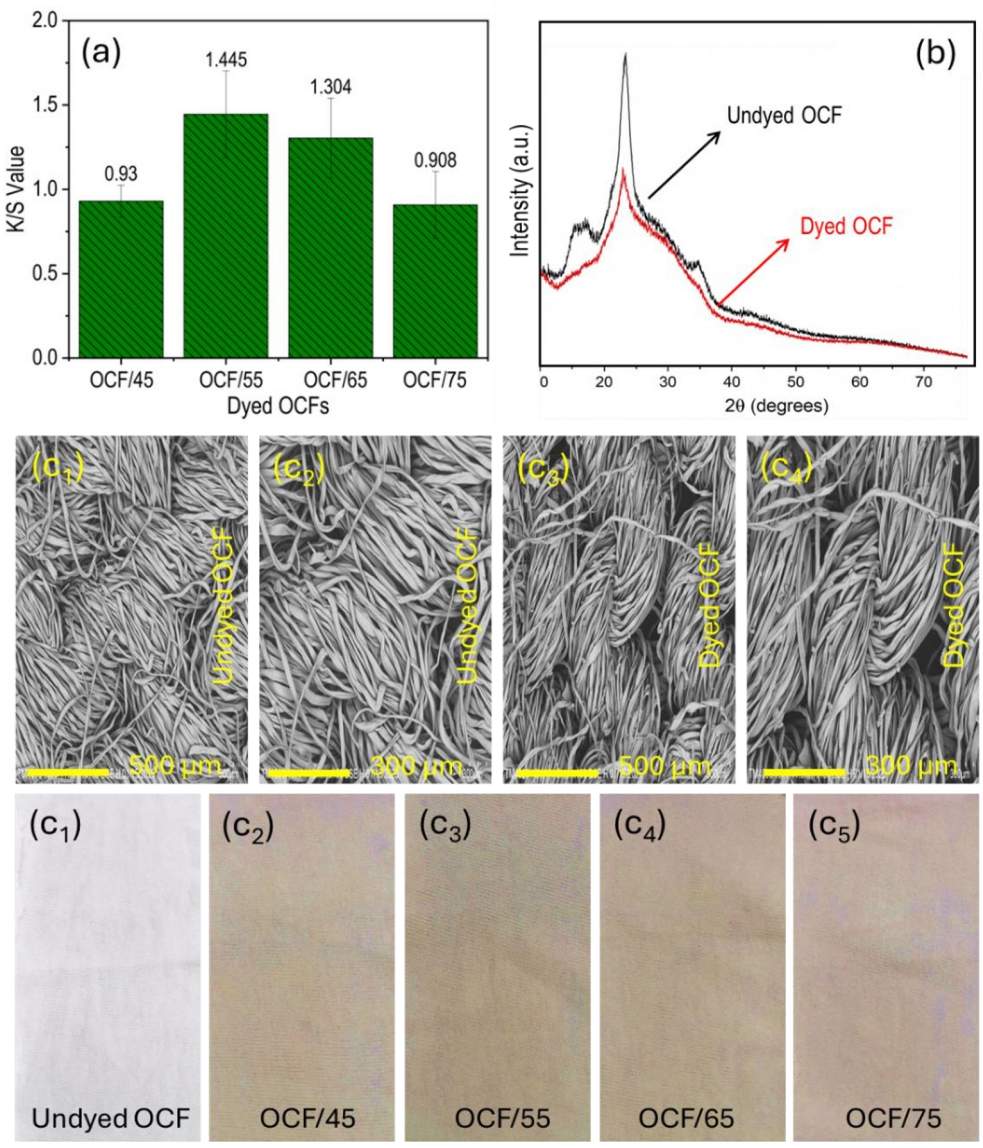

Figure 2. (a) Color strength (K/S) of OCF dyed at different temperatures. (b) XRD patterns, and (c) SEM images of dyed and undyed OCF. (d) Photographs of undyed and dyed OCF samples at varying temperatures.

The endogenous dyeing mechanism of tea-based phytochemicals (**Figure 1b**) onto cotton involves primarily hydrogen bonding, π–π stacking, and possible covalent and coordination interactions [18]. Polyphenols such as tannic acid (a hydrolyzable tannin) contain multiple phenolic hydroxyl groups that interact with cellulose chains via hydrogen bonds [19]: Cell–OH···HO–Ar (hydroxyl groups of cellulose interacting with phenolic –OH). Under mildly acidic to neutral conditions, tannic acid may undergo partial oxidation, forming quinones, which can react with nucleophilic –OH groups of cellulose through Michael-type addition [20]: Ar–C=O + Cell–OH → Ar–C–O–Cell (covalent bonding via nucleophilic addition to oxidized quinones). Furthermore, metal ions naturally present or introduced (which have been avoided in this study) may facilitate coordination complex formation between tannin moieties and cellulose [21]: [Ar–OH]–Fe^{3+}–[Cell–OH] (metal–ligand bridges enhancing fixation). The overall chemical interaction is shown in **Figure 1**b. These synergistic interactions result in stable dye-fiber assemblies, enhancing color fastness and dye uptake efficiency.

4 Conclusion

This study successfully establishes a sustainable, mordant-free dyeing method for organic cotton using green tea waste extracts. Ultrasonic-assisted dyeing at 55 °C optimizes polyphenolic dye uptake, yielding vibrant, durable coloration with excellent fastness properties. Structural and morphological analyses confirmed enhanced dye-fiber interactions and transient disruption of cellulose crystallinity, facilitating deep dye penetration without fiber damage. By transforming agro-industrial waste into a value-added product, this approach addresses environmental challenges posed by synthetic dyes and supports circular economic principles. Our findings highlight the potential of green tea waste as a low-cost, eco-friendly natural dye, advancing sustainable textile processing and waste valorization.

Declaration of Competing Interest. The authors declare no competing interests. Generative AI tools were used solely to enhance language and readability. All content was subsequently reviewed and edited by the authors, who take full responsibility for the final version.

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References:

[1] K. M. Albalawi *et al.*, "Hydrothermal assisted α-amylase-modified silver nanoparticles (α-Amy-AgNPs): Multi-functional nanocatalyst for dye degradation and biomedical applications," *J. Water Process Eng.*, vol. 77, p. 108460, Sep. 2025, doi: 10.1016/j.jwpe.2025.108460.

[2] K. Singha, P. Pandit, S. Maity, and S. R. Sharma, "Chapter 11 - Harmful environmental effects for textile chemical dyeing practice," in *Green Chemistry for Sustainable Textiles*, N. Ibrahim and C. M. Hussain, Eds., in The Textile Institute Book Series. , Woodhead Publishing, 2021, pp. 153–164. doi: 10.1016/B978-0-323-85204-3.00005-1.

[3] S. S. Affat, "Classifications, Advantages, Disadvantages, Toxicity Effects of Natural and Synthetic Dyes: A review," *Univ. Thi-Qar J. Sci.*, vol. 8, no. 1, pp. 130–135, May 2021.

[4] N. Habib, S. Adeel, A. Ali, R. Mia, S. R. Khan, and M. A. Qayyum, "Ultrasonic-assisted sustainable pollution free advanced method for isolation of colouring material from Amba Haldi (*Curcuma aromatica*) for wool dyeing," *Sci. Prog.*, vol. 106, no. 3, p. 00368504231188610, Jul. 2023, doi: 10.1177/00368504231188610.

[5] H. Jiang *et al.*, "Eco-friendly dyeing and finishing of organic cotton fabric using natural dye (gardenia yellow) reduced-stabilized nanosilver: full factorial design," *Cellulose*, vol. 29, no. 4, pp. 2663–2679, Mar. 2022, doi: 10.1007/s10570-021-04401-9.

[6] E. O. Alegbe and T. O. Uthman, "A review of history, properties, classification, applications and challenges of natural and synthetic dyes," *Heliyon*, vol. 10, no. 13, p. e33646, Jul. 2024, doi: 10.1016/j.heliyon.2024.e33646.

[7] M. A. Habib, M. N. Pervez, S. Mahmud, M. M. R. Khan, and Q. Heng, "Macadamia integrifolia: A new source of natural dyes for textile colouration," *Asian J. Chem.*, vol. 29, no. 7, pp. 1543–1548, May 2017, doi: 10.14233/ajchem.2017.20560.

[8] H. Jiang *et al.*, "Fabrication and stabilization of green nanosilver using gardenia yellow natural dyes for efficient degradation of bacteria," *Environ. Prog. Sustain. Energy*, vol. 42, no. 3, p. e14048, 2023, doi: 10.1002/ep.14048.

[9] N. M. N. 'Aqilah, K. Rovina, W. X. L. Felicia, and J. M. Vonnie, "A Review on the Potential Bioactive Components in Fruits and Vegetable Wastes as Value-Added Products in the Food Industry," *Molecules*, vol. 28, no. 6, p. 2631, Jan. 2023, doi: 10.3390/molecules28062631.

[10] D. Seth *et al.*, "Sustainable environmental practices of tea waste—a comprehensive review," *Environ. Sci. Pollut. Res.*, vol. 32, no. 12, pp. 7449–7467, Mar. 2025, doi: 10.1007/s11356-023-30848-3.

[11] Sukemi, K. Pratumyot, C. Srisuwannaket, N. Niamnont, and W. Mingvanish, "Dyeing of cotton with the natural dye extracted from waste leaves of green tea (Camellia sinensis var. assamica)," *Color. Technol.*, vol. 135, no. 2, pp. 121–126, 2019, doi: 10.1111/cote.12381.

[12] H. Xu and H. Song, "A Systematic Review of Tea Dyeing in the Textile Industry: Research Trends, Dyeing Performance, Functional Characteristics, and Application Potential," *AATCC J. Res.*, vol. 12, no. 1, p. 24723444251314916, 2025.
[13] S. Mahmud, Md. N. Pervez, M. A. Taher, K. Mohiuddin, and H.-H. Liu, "Multifunctional organic cotton fabric based on silver nanoparticles green synthesized from sodium alginate," *Text. Res. J.*, vol. 90, p. 004051751988753, Nov. 2019, doi: 10.1177/0040517519887532.
[14] Y. Zhang, Q. Zhou, W. Xia, L. J. Rather, and Q. Li, "Sonochemical mordanting as a green and effective approach in enhancing cotton bio natural dye affinity through soy surface modification," *J. Clean. Prod.*, vol. 336, p. 130465, Feb. 2022, doi: 10.1016/j.jclepro.2022.130465.
[15] A. D. T. Phan, B. R. D'Arcy, and M. J. Gidley, "Polyphenol–cellulose interactions: effects of pH, temperature and salt," *Int. J. Food Sci. Technol.*, vol. 51, no. 1, pp. 203–211, Dec. 2015, doi: 10.1111/ijfs.13009.
[16] L. Lambrecht, L. Capablanca, E. Bou-Belda, I. Montava, P. Díaz-García, and J. Gisbert-Payá, "Enhancing Polyphenols and Tannins Concentration on Cotton Dyed with Red Tea," *Sustainability*, vol. 15, no. 4, p. 3062, Jan. 2023, doi: 10.3390/su15043062.
[17] Y. Zhang, Shahid-ul-Islam, L. J. Rather, and Q. Li, "Recent advances in the surface modification strategies to improve functional finishing of cotton with natural colourants - A review," *J. Clean. Prod.*, vol. 335, p. 130313, Feb. 2022, doi: 10.1016/j.jclepro.2021.130313.
[18] X. Zhai *et al.*, "Investigation on dyeing mechanism of modified cotton fiber," *RSC Adv.*, vol. 12, no. 49, pp. 31596–31607, 2022, doi: 10.1039/D2RA05668B.
[19] S. Basak, A. S. M. Raja, S. Saxena, and P. G. Patil, "Tannin based polyphenolic bio-macromolecules: Creating a new era towards sustainable flame retardancy of polymers," *Polym. Degrad. Stab.*, vol. 189, p. 109603, Jul. 2021, doi: 10.1016/j.polymdegradstab.2021.109603.
[20] C. Heinritz, X. J. Ng, and T. Scheibel, "Bio-inspired Protein-Based and Activatable Adhesion Systems," *Adv. Funct. Mater.*, vol. 34, no. 35, p. 2303609, 2024, doi: 10.1002/adfm.202303609.
[21] M. T. Islam, M. L. R. Liman, M. N. Roy, M. M. Hossain, M. R. Repon, and M. A. A. Mamun, "Cotton dyeing performance enhancing mechanism of mangiferin enriched bio-waste by transition metals chelation," *J. Text. Inst.*, Mar. 2022, Accessed: Aug. 25, 2025. [Online]. Available: https://www.tandfonline.com/doi/abs/10.1080/00405000.2021.1892337