Research Article

Journal of Environmental Nanotechnology

A Sustainable Technique to Enhance the Color Intensity of Natural Dyes on Cotton Fabric

K. Swetha* and S. Karpagam Chinnammal

Department of Costume Design and Fashion, Chikkanna Government Arts College, Tiruppur, TN, India

Received: 24.05.2024 Accepted: 19.06.2024 Published: 30.06.2024

*swethakitchappan@gmail.com

ABSTRACT

Natural dyeing of cotton, as opposed to its synthetic counterpart, offers a multitude of benefits that extend far beyond aesthetics. While it imparts unique value to fabrics, its true significance lies in its contribution to environmental sustainability, human health, and cultural preservation. The bark of purple orchid (*Bauhinia purpurea*), harbors a natural pigment that contributes as a natural dye. Custard apple rind extracts, rich in tannins and other active compounds, have been documented to effectively mordant various fabrics, including cotton. This eco-friendly option offers a sustainable alternative to conventional, often metal-based mordants, potentially reducing environmental impact. Optimum results were achieved with the pre-treatment using casein (8%) and 0.5 part of K_2CO_3 to 1 part of casein. The pre-treated and pre-mordanted fabric was dyed at 80 °C at 12% concentration for 60 minutes. The colour of each dyed material was investigated in terms of the CIELAB (L^*, a^*, and b^*) and K/S values.

Keywords: Sustainable; Natural dyeing; Casein; Eco-friendly; Colour depth.

1. INTRODUCTION

Indian supremacy in cotton dyeing, probably resulted from the country's early settlement, its large population and labour force, and the presence of wild cotton, the best of the dye-bearing plant, and the necessary natural metal mordants. In addition, the Indians' unusual love of colour and patient, perfectionistic approach to life, probably contributed to their pre-eminence among the ancients. No important or specified information was with them to use the natural colours available near to them. From that period on, this art and its important component, natural dye, has improved itself in terms of stability, shades, and its working archetype until the invention of natural dye's strongest rival "synthetic dye." Most industrially produced synthetic dyes are azo dyes, which might get converted to cancer-causing compounds under anaerobic conditions, adding to the severity. Additionally, they are highly toxic and not susceptible to degradation due to their complex structure. Furthermore, synthetic dye intermediates are responsible for causing water pollution, as cautioned by organizations such as Global Organic Textile Standards (GOTS), Food and Agriculture Organization (FAO), and Environmental Protection Agencies (EPA) (Shahid *et al.* 2013). Natural dyes haven't seen a silver lining until slowly but steadily, new-age customers began to recognize the importance of natural dyes as a "revival of new optimism" in terms of acknowledgment of new and earthy shades provided by natural colours. (Vankar *et al.* 2019).

As one of the four natural fibres in the textile industry, cotton fibre has the characteristics of comfort, softness, and warmth, occupying a large part of the natural textiles (Wakelyn, 2006). Cotton is a type of cellulosic fiber that is made of a linear chain of D-glucose units linked by several hundred to over ten thousand β (1 → 4) links. Cellulose depends on hydrogen bonding, intermolecular interactions, and other non-specific interactions to form a highly crystalline zone that makes dyeing cotton fibers or fabrics with natural dyes more difficult. Cotton fiber has the molecular formula ($C_6H_{10}O_5$) n, where the mass fraction of oxygen is 49.39%, hydrogen is 6.17%, and carbon is 44.44% (Wakelyn, 2006). The monomer of the cotton fibre is dehydrated D-glucopyranose-type, which contains only hydroxyl groups and ether bonds having high negative surface density. This high negative charge density is not favourable for dyeing processes with negatively charged polyphenolic dyes, resulting in a lower dyeing rate and colour fastness properties. Hence, when dyeing the cotton with natural dyes, it is necessary to minimize the repulsive forces, which can be achieved by mordanting with metal salts and bio-mordants (Zhang *et al.* 2022).

Bio-mordants such as Annona squamosa (custard apple rind) can be considered as phytochemical compound sources. Custard apple rind contains many biological phenolic compounds, including alkaloids, tannins, flavonoids, and saponins, which have antioxidant properties and can scavenge free radicals (Nguyen *et al.* 2023).

Bauhinia purpurea belongs to the family of Fabaceae and is commonly known as camel's foot tree or purple orchid tree (Zakaria *et al.* 2011) B. purpurea reported the presence of various phytochemical constituents. It contains glycosides, saponin, phenolic compounds, tannins, flavonoids, fixed oils, flavones glycoside, alkaloids, sterol, steroids, flavanones, lutein, beta-sitosterol, etc (Chanchal *et al.* 2015). The bark also contains a wide range of chemical compounds, including 5,6-Dihydroxy-7-methoxyflavone 6-O-beta-D-xylopyranoside. Cotton fabrics were pretreated with whey protein isolate (WPI) to improve their dyeability toward a tannin-rich natural dye obtained from Xylocarpus granatum bark (Pisitsak *et al*. 2016).

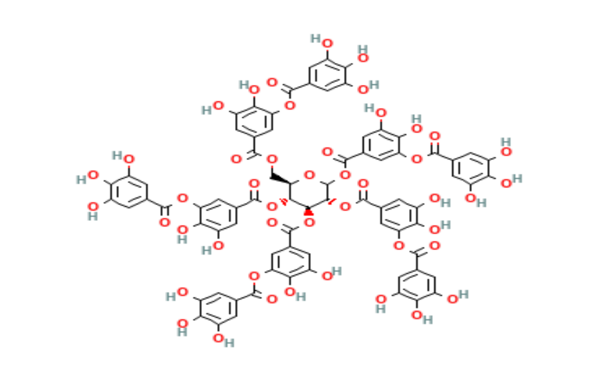


Fig. 1: Structure of tannin

Although the casein protein component of milk lacks a well-defined secondary and tertiary structure, it is composed of various proteins with distinct functions (Bhat *et al.* 2016). Four primary casein types account for about 80% of the total protein content of cow's milk: The caseins α-s1, α-s2, β and κ (Chevrier *et al.* 2016). Casein is proposed to be the main protective constituent in milk. Casein is an amphiphilic protein (Chen *et al.* 2013). Although most of the casein applications are in the food sector, there are several non-food-related applications of casein (Audic *et al.* 2010). Casein has also been impactful due to its biocompatibility, biodegradability, and higher availability. Potassium carbonate(K_2CO_3) also known as potash, pearl ash, salt of tartar, or carbonate of potash is a base and is eco-friendly (He *et al.* 2015; Lv *et al.* 2023) Potassium carbonate has several advantages, especially regarding its environmental sustainability, toxicity, physiochemical properties, and costs (Gohla *et al.* 2021).

2. MATERIALS AND METHODS

2.1 Materials

The bark of the purple orchid tree was used as dye source and custard apple rind was used as a mordant, and was obtained from Tiruppur. Bleached, 100% cotton fabric was sourced from Venkateshwara textile, Erode; Casein from bovine milk (quality level-200 and assay-87-94% protein basis) was obtained from Sigma Aldrich, Bangalore; Potassium carbonate and sodium bicarbonate were purchased from Tiruppur Scientific and Fed-ash (mod) was procured from Sarex chemicals, Mumbai. These were used as received without any modifications.

Fig. 2: Bark of Purple orchid

Fig. 3: Custard apple rind

2.2 Methods

2.2.1 Pilot Study

2.2.1.1 Pre-treatment with Casein

The casein powder is insoluble in water. Thus, base is needed to dissolve it. Sodium bicarbonate, Fed-ash(mod) (sodium carbonate) and potassium carbonate were used individually to dissolve casein in water (material to liquor ratio of 1:20). To further assist in complete dissolution, water was heated to 40 °C. Bases and casein were added into a beaker containing water and stirred using a magnetic stirrer until the casein was completely dissolved. Water turned slightly opaque; the fabric was then allowed to soak for 12 hours.

2.2.1.2 Pre-mordanting and Dyeing

Both the custard apple (CA) rind and purple orchid (PO) bark were dried, powdered, and sieved to a fine powder separately. Custard apple rind powder was mixed with the required quantity of water and heated.

Casein-treated fabric was immersed in the mordanting liquor and heated at 80°C for 60 minutes. The fabric was taken out, excess water removed, soaked in dye liquor (PO bark) and heated at 80°C for 60 minutes. The dyed fabric was removed from the dye bath, rinsed, and dried. Cotton fabric that is pre-mordanted and dyed without pre-treatment of casein was used as control sample.

Table 1. Parameters for application of casein

Material	Concentration	MLR	Time	Temperature
Casein	10 %	1:20	12 hours (Soak)	40 °C
Bases	1:1 (casein: base)			

Table 2. Parameters for application of mordant and dye

Material	Concentration	MLR	Time	Temperature
Mordant (CA rind)	12%	1:40	60 minutes	80 °C
Dye (PO rind)	12%	1:40	60 minutes	80 °C

2.2.1.3 Selection of Base

The fabric pre-treated with casein, mordant, and dyed was visually evaluated based on colour intensity and evenness. Out of three bases (potassium carbonate / Fed-ash(mod) / sodium bi-carbonate), fabric treated with potassium carbonate showed better results when compared to the other two bases and was selected for further study.

2.2.2 Actual Study

2.2.2.1 Optimization of Casein and Potassium Carbonate

8%, 10% and 12% casein (o.w.f), 0.5, 1 and 1.5 parts potassium carbonate (on weight of casein) were used. The fabric was pretreated with casein, pre-mordanted, and dyed as per the procedure done in the pilot study. In this process, a total of 9 samples was obtained and tested for colour depth and colour difference.

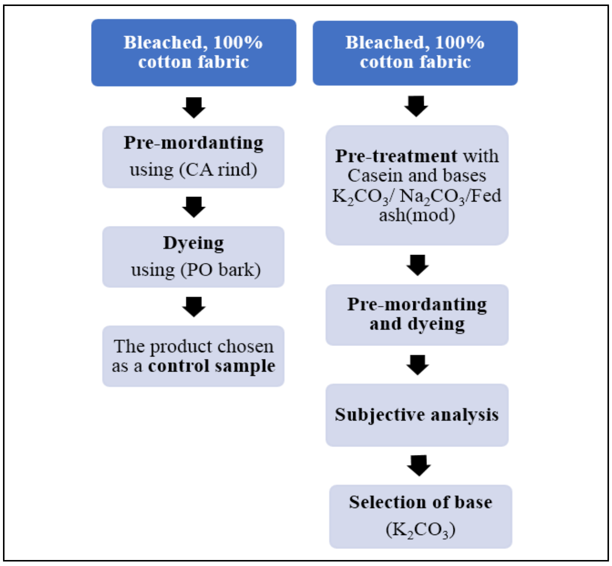


Fig. 4: Pilot study flowchart

Table 3: Parameters for actual study

PRE-TREATMENT					
CASEIN (O.W.F)	POTASSIUM CARBONATE (ON WEIGHT OF CASEIN)	PARAMETERS		SAMPLE CODE	PARAMTERS FOR MORDANTING AND DYEING
8%	0.5	MLR **1:20**	→	C8P05	CONCENTRATION **12%**
	1		→	C8P1	
	1.5		→	C8P15	
10%	0.5		→	C10P05	MLR **1:40**
	1	TEMPERATURE **40°C**	→	C10P1	
	1.5		→	C10P15	TEMPERATURE **80°C**
12%	0.5		→	C12P05	
	1	TIME **12 HOURS**	→	C12P1	TIME **60 MINUTES**
	1.5		→	C12P15	

2.2.2.2 Evaluation of Colour Depth

The colour strength (K/S) and CIELAB of the dyed samples were assessed using colorspace CIELAB(1976), with a 10° observer, D65 illuminant and spectro of 5100. 420 is the maximum wavelength used in this testing in order to assess dyeing performance. Colour strength is a measure of the ability of a dye to impart colour to materials.

The colour strength is evaluated by light absorption in the visible region of the spectrum. Relative colour strength can be defined as the ratio of K/S values for samples compared to a standard at the same wavelength, expressed as a percentage. 'K' and 'S' are the absorption and scattering coefficients of the dyed sample. Relative colour strength (%) is calculated from reflectance, R using the Kubelka-Munk equation as follows (Hossain *et al*. 2018):

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

The color difference is expressed as ΔE* and is calculated by the following Eq. (1):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (1)$$

Where, E* is the CIELAB color difference between batch and standard. Here L*, a*, b* and hence E* are in commensurate units. L* represents the difference between lightness (where L* = 100) and darkness (where L* = 0), a* the difference between green (−a*) and red (+a*) and b* the difference between yellow (+b*) and blue (−b*).

3. RESULTS AND DISCUSSION

The application of casein with potassium carbonate improved the colour depth which was proved by the evaluation of colour difference and colour depth. The colour strength and colour difference were higher in the fabric (C8P05) that was treated with 8% casein and 1:0.5 weight of potassium carbonate (on the weight of casein) followed by 8% of casein and 1.5 times potassium carbonate treated fabric (C8P15). The fabric (C10P1) treated with 10% casein and equal weight of potassium carbonate to casein resulted in poor performance. The rest of the fabric delivered average results. It is clearly evident from Table 4 and Figure 6 that out of 8, 10 and 12% concentration of casein, fabric pre-treated with 8% casein gave better results. Also, from Fig. 7, it is observed that 0.5 times potassium carbonate gave better results with 8 and 10% concentration of casein. In 12% casein, 0.5, 1- and 1.5-times potassium carbonate produced similar values.

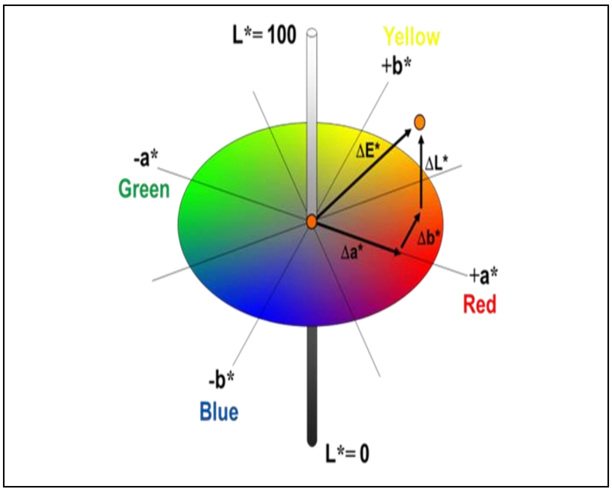
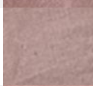
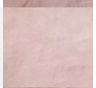
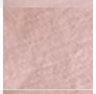


Fig. 5: The CIELAB color space

Table 4. Colour depth and colour difference values with color coordinates

Sample Code	Weight of Casein	Weight of casein : Weight of K_2CO_3	Colour coordinates L*	a*	b*	c*	h*	ΔE value	K/S Value	Sample
C8P05	8%	1:0.5	68.292	13.555	12.156	18.207	41.869	7.954	0.8803	
C8P1		1:1	69.683	11.107	9.576	14.665	40.750	5.819	0.7145	
C8P15		1:1.5	68.200	10.290	10.530	14.723	45.642	7.049	0.8633	
C10P05	10%	1:0.5	70.799	11.611	10.624	15.738	42.441	6.154	0.6874	
C10P1		1:1	72.504	8.749	8.699	12.338	44.818	3.323	0.5699	
C10P15		1:1.5	70.516	9.375	9.175	13.118	44.364	5.219	0.667	
C12P05	12%	1:0.5	70.751	10.450	9.769	14.305	43.054	5.523	0.6707	
C12P1		1:1	70.283	9.845	9.475	13.664	43.885	5.433	0.684	
C12P15		1:1.5	70.351	9.178	9.088	12.916	44.700	5.634	0.7299	

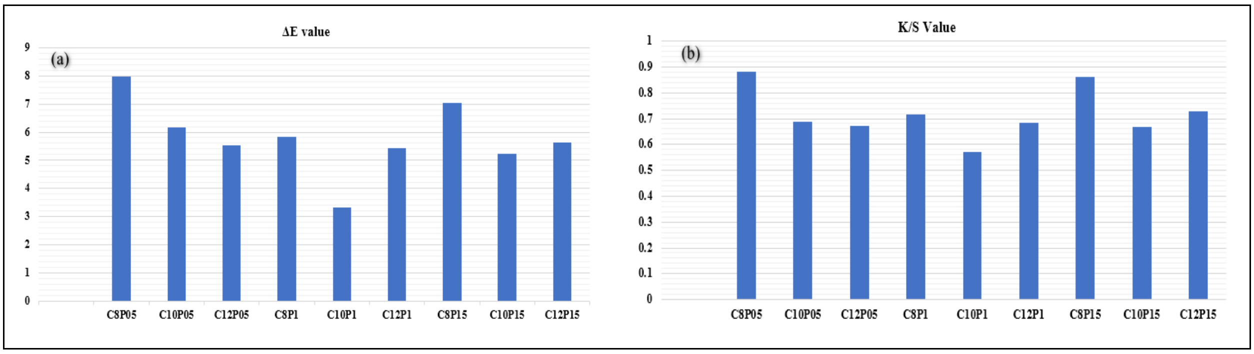


Fig 6: (a & b): Values of colour difference and colour depth based on concentration of casein

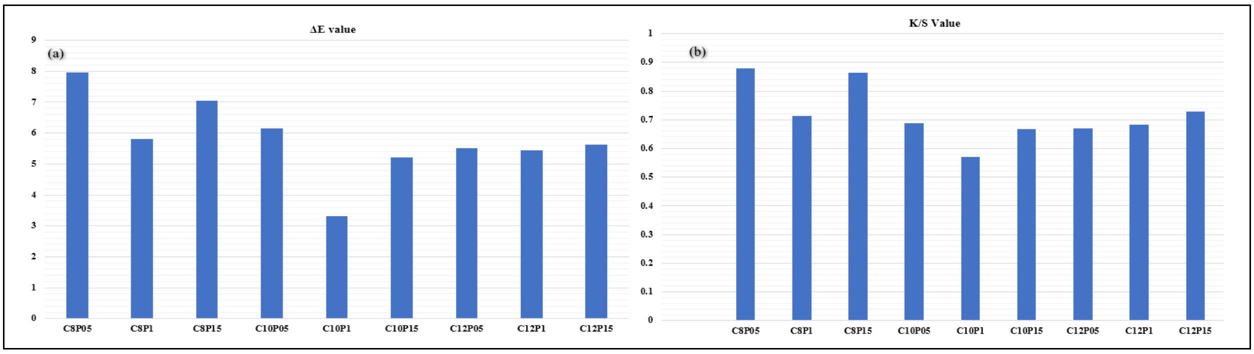


Fig. 7: (a & b): Values of colour difference and colour depth based on concentration of potassium carbonate

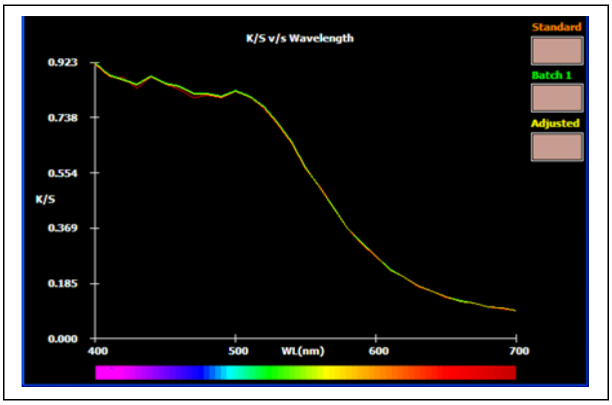


Fig. 8: Graph showing K/S v/s Wavelength of C8P05

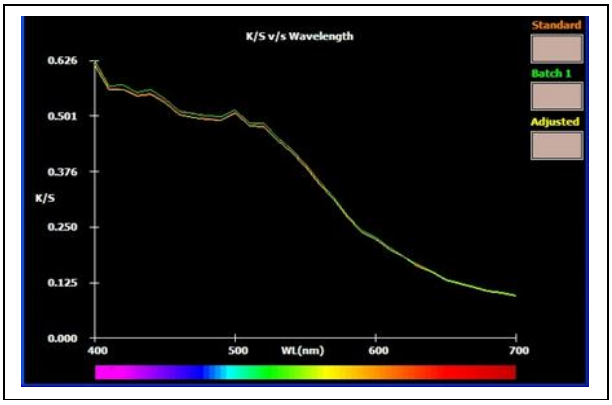


Fig. 10: Graph showing K/S v/s Wavelength of C10P1

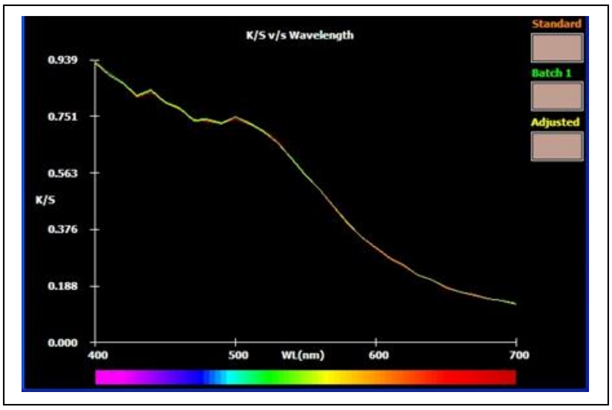


Fig. 9: Graph showing K/S v/s Wavelength of C8P15

4. CONCLUSION

This study has demonstrated the effectiveness of natural dyeing with purple orchid bark and custard apple rind as mordant in achieving colors on textiles. The application of casein, a protein binder, along with potassium carbonate, further enhanced the color depth and produced a color difference compared to using the mordant alone. In this study, the sample treated with the concentration of 8% casein (o.w.f) and 0.5 times potassium carbonate (on weight of casein) (C8P05) achieved the highest colour depth(0.8803) and colour difference (7.954).These findings suggest the potential of this natural dyeing approach for sustainable and eco-friendly textile coloration. Further research could explore optimizing the dyeing process for different fabric types and mordant concentrations to achieve a wider range of colors and improve colorfastness properties. Additionally, investigating the scalability of this technique for commercial applications would be valuable for promoting the use of natural dyes in the textile industry.

FUNDING

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

REFERENCES

Audic, J. L., Chaufer, B., Applications of milk components in products other than foods, In: Improving the Safety and Quality of Milk. Elsevier, pp 475–489 (2010). https://doi.org/ 10.1533/9781845699437.3.475

Bhat, M. Y., Dar, T. A., Singh, L. R., Casein Proteins: Structural and Functional Aspects, In: Milk Proteins - From Structure to Biological Properties and Health Aspects. InTech (2016). https://doi.org/ 10.5772/64187

Chanchal, D. K., Niranjan, P., Alok, S., Saurabh, S. S. and, An Update on Ayurvedic Herb Kachhnar (Bauhinia Purpurea Linn.)- A review, *Int. J. Pharmacogn.* 2(8), 381–390 (2015). https://doi.org/10.13040/IJPSR.0975-8232.IJP.2(8).381-390

Chen, L., Wu, X., Chen, X. D., Comparison between the digestive behaviors of a new in vitro rat soft stomach model with that of the in vivo experimentation on living rats – Motility and morphological influences, *J. Food Eng.* 117(2), 183–192 (2013). https://doi.org/10.1016/j.jfoodeng.2013.02.003

Chevrier, G., Mitchell, P., Beaudoin, M.-S., Marette, A., Impact of Dietary Proteins on Energy Balance, Insulin Sensitivity and Glucose Homeostasis, In: The Molecular Nutrition of Amino Acids and Proteins. Elsevier, pp 241–264 (2016). https://doi.org/10.1016/B978-0-12-802167-5.00018-9

Gohla, J., Bračun, S., Gretschel, G., Koblmüller, S., Wagner, M., Pacher, C., Potassium carbonate (K2CO3) – A cheap, non-toxic and high-density floating solution for microplastic isolation from beach sediments, *Mar. Pollut. Bull.* 170, 112618 (2021). https://doi.org/10.1016/j.marpolbul.2021.112618

He, D., Peng, Z., Gong, W., Luo, Y., Zhao, P., Kong, L., Mechanism of a green graphene oxide reduction with reusable potassium carbonate, *RSC Adv.* 5(16), 11966–11972 (2015). https://doi.org/10.1039/C4RA14511A

Lv, L., Huang, S., Zhou, C., Ma, W., Biochar activated by potassium carbonate to load organic phase change material: Better performance and environmental friendliness, *Ind. Crops Prod.* 204, 117184 (2023). https://doi.org/10.1016/j.indcrop.2023.117184

McLean, B. W., Bray, M. R., Boraston, A. B., Gilkes, N. R., Haynes, C. A., Kilburn, D. G., Analysis of binding of the family 2a carbohydrate-binding module from Cellulomonas fimi xylanase 10A to cellulose: specificity and identification of functionally important amino acid residues, *Protein Eng. Des. Sel.* 13(11), 801–809 (2000). https://doi.org/10.1093/protein/13.11.801

Nguyen, T. T., Phan, T. H., Stirred maceration extraction of custard apple (Annona squamosa L.) peel, *IOP Conf. Ser. Earth Environ. Sci.* 1155(1), 012016 (2023). https://doi.org/10.1088/1755-1315/1155/1/012016

Pisitsak, P., Hutakamol, J., Thongcharoen, R., Phokaew, P., Kanjanawan, K. and Saksaeng, N., Improving the dyeability of cotton with tannin-rich natural dye through pretreatment with whey protein isolate, *Ind. Crops Prod.*, *79*, 47–56 (2016). https://doi.org/10.1016/j.indcrop.2015.10.043

Hossain, A., Samanta, A. K., Bhaumik, N. S., Vankar, P. S., and Shukla, D., Non-toxic Coloration of Cotton Fabric using Non-toxic Colorant and Nontoxic Crosslinker, *J. Text. Sci. Eng.*, 08(05) (2018). https://doi.org/10.4172/2165-8064.1000374

Shahid, M., Shahid-ul-Islam, Mohammad, F., Recent advancements in natural dye applications: a review, *J. Clean. Prod.* 53, 310–331 (2013). https://doi.org/10.1016/j.jclepro.2013.03.031

Vankar, P. S., Shukla, D., New Trends in Natural Dyes for Textiles, New Trends in Natural Dyes for Textiles, Elsevier (2019). https://doi.org/ 10.1016/C2017-0-03994-0

Wakelyn, P. J., Cotton Fiber Chemistry and Technology. Cotton Fiber Chemistry and Technology, *CRC Press*, (2006).
https://doi.org/ 10.1201/9781420045888

Zakaria, Z. A., Abdul Hisam, E. E., Rofiee, M. S., Norhafizah, M., Somchit, M. N., Teh, L. K., Salleh, M. Z., In vivo antiulcer activity of the aqueous extract of Bauhinia purpurea leaf, *J. Ethnopharmacol.*, 137(2), 1047–1054 (2011).
https://doi.org/10.1016/j.jep.2011.07.038

Zhang, Y., Shahid-ul-Islam, Rather, L. J., Li, Q., Recent advances in the surface modification strategies to improve functional finishing of cotton with natural colourants - A review, *J. Clean. Prod.*, 335, 130313 (2022).
https://doi.org/10.1016/j.jclepro.2021.130313