SUSTAINABLE CELLULOSIC FIBROUS SUBSTRATE DYEING USING *CALENDULA OFFICINALIS* PETAL EXTRACT: COLORIMETRIC AND FASTNESS PROPERTIES EVALUATION

POPOVICI Lucia-Florina[1], COMAN Diana[2], OANCEA Simona[1], COMAN Andrei[3]

[1] "Lucian Blaga" University of Sibiu, Faculty of Agricultural Sciences, Food Industry and Environmental Protection, 550012, 7-9 Dr. I. Ratiu Street, Sibiu, Romania, E-Mail: luciaflorina.popovici@ulbsibiu.ro, simona.oancea@ulbsibiu.ro

[2] "Lucian Blaga" University of Sibiu, Romania, Faculty of Engineering, 550024, 10 Victoriei Blvd, Sibiu, Romania, Email: diana.coman@ulbsibiu.ro

[3] Medical Practice Comosan SRL, Sibiu, Romania, Email: dr.comanandrei@gmail.com

Corresponding author: Popovici Lucia-Florina, E-mail: luciaflorina.popovici@ulbsibiu.ro

Abstract: *Natural dyeing of cellulosic supports intended for hygienic and medical use is increasingly explored as a sustainable alternative to conventional coloration. In the present study, cotton samples were dyed with Calendula officinalis flower extract by two technological routes, exhaustion and ultrasonication, combined with two mordanting strategies: simultaneous mordanting and premordanting. Citric acid, tannic acid, oxalic acid, $CuSO_4$ + oxalic acid, and $FeSO_4$ + oxalic acid were applied at 10% owf. The chromatic response of the dyed fabrics was assessed through the CIELAB descriptors ΔL^*, Δa^*, Δb^*, ΔC^*, ΔH^* and ΔE^*, while durability was estimated through color fastness properties to acidic and alkaline perspiration and to dry and wet rubbing. The experimental matrix showed that most samples preserved a yellow to yellow-brown domain, whereas metal-assisted systems, especially $FeSO_4$ + oxalic acid, promoted greener or olive-like deviations together with the largest color differences. Premordanting generally intensified the chromatic modification relative to simultaneous mordanting, most markedly under exhaustion. Among the biomordants, citric acid maintained shades closest to the reference sample, while tannic acid offered a favorable balance between color enrichment and fastness. The best resistance values were recorded for $CuSO_4$ + oxalic acid and $FeSO_4$ + oxalic acid systems, whereas dry rubbing fastness was consistently superior to wet rubbing fastness, which still remains satisfactory. These results support the feasibility of Calendula-based eco-dyeing for cotton fabrics requiring moderate to good service performance and a reduced chemical footprint, such as those intended for disposable medical items.*

Key words: *natural dye, cotton fabrics, biomordants, ultrasonication, CIELAB, medical textiles*

1. INTRODUCTION

The replacement of synthetic dyes with plant-derived colorants has become a major direction in sustainable textile processing, because natural dyes are renewable, generally less hazardous, and compatible with circular-economy strategies when appropriate biomass resources are selected [1,2]. However, natural dyes still face important limitations related to shade reproducibility, fixation efficiency, and fastness, especially on cellulosic fibers such as cotton, where dye–fiber affinity is often weaker than on protein substrates [2,3]. For this reason, mordanting remains a key step in natural dyeing, particularly when the target is to obtain deeper shades or improved resistance to use-related stresses.

Calendula officinalis L. (*C. officinalis)* is a valuable botanical resource due to its rich content in carotenoids, flavonoids and other bioactive constituents, which also account for its traditional medicinal and cosmetic uses [4]. Beyond pharmaceutical applications, *C. officinalis* flowers have attracted growing interest as a natural dye source capable of producing yellow to orange chromatic domains on natural fibres [4,5,6]. In addition, ultrasound-assisted textile processing has emerged as a promising route for reducing dyeing temperature, time, and chemical consumption while still promoting mass transfer and dye uptake [7].

The objective of the present study was to comparatively evaluate two *C. officinalis* dyeing routes applied to cellulosic textile supports, exhaustion and ultrasonication, combined with simultaneous mordanting or premordanting. The comparison was performed through CIELAB descriptors and color fastness properties to perspiration and rubbing, with the aim of identifying the most promising eco-dyeing conditions for cotton materials with possible medical or hygienic use.

2. MATERIALS AND METHODS

2.1. Preparation of Extract

Petals of *C. officinalis* were collected from a garden of Sibiu region, Romania. After collection, petals were dried at 50 °C, until moisture content reached 5%. Finely powdered *C. officinalis* petals, obtained using a Grindomix mill (Grindomix GM 200, Retsch, Germany), were subjected to extraction with 70% aqueous ethanol using a solid-to-solvent ratio of 1:15 (w/v). Extraction was carried out for 24 h at room temperature. Subsequently, the hydroethanolic extract was concentrated under vacuum at 50 °C to approximately 50% of its initial volume using a rotational vacuum concentrator (RVC 2-18 CDplus, Martin Christ, Germany).

2.2. Materials Used for Textile Dyeing

The textile material used as support was a 100% cotton fabric, with a basis weight of 145 g/m², a plain weave structure, and a threads fineness of 34/1Nm. All chemicals used in the dyeing experiments were of analytical grade, with purities higher than 98%.

Two application variants were investigated: simultaneous mordanting (Variant 1), in which the mordant was added directly to the dye bath together with the *C. officinalis* extract, and premordanting (Variant 2), in which the cotton samples were first treated with the mordanting solution and subsequently dyed. In both variants, dyeing was performed by two methods, conventional exhaustion and ultrasonic-assisted dyeing, and included unmordanted reference samples. The same mordanting formulations were used throughout the study: citric acid, tannic acid, oxalic acid, $CuSO_4$ + oxalic acid, and $FeSO_4$ + oxalic acid, each used at 10% relative to the mass of textile material. For the dyeing stage, the liquor ratio was 1:25. Exhaustion dyeing was carried out for 20 min at 80°C, whereas ultrasonication was performed for 15 min at 40°C. For the premordanting step, the liquor ratio was 1:20 before the subsequent application of the extract.

2.3. Fastness Properties to Perspiration and Rubbing

Color fastness to perspiration was evaluated according to Romanian standard in force SR EN ISO 105-E04:2013 (reconfirmed in 2023), using both acidic and alkaline artificial perspiration solutions. The composite specimens were impregnated at a liquor ratio of 50:1 for 30 min, squeezed, and placed under a nominal pressure of (12.5 ± 0.9) kPa between the plates of the testing device. The samples were then maintained at 37 ± 2 °C for 4 h. After testing, the change in color and staining were assessed using the grey scale for color change/staining, with ratings from 1 to 5, where 5 indicates the highest fastness and 1 the lowest.

Rubbing fastness was evaluated under both dry and wet conditions according to ISO 105-X12:2016, using CrockMaster equipment (James Heal, UK) in order to assess the resistance of the dyed cotton samples to color transfer during mechanical action. The results were expressed on the grey scale from 1 to 5, where 5 corresponds to the best fastness.

2.4. Chromatic Characterization of Dyed Cotton in the CIELAB System

The chromatic data modifications of the dyed cotton samples was performed in the CIELAB color space by determining the parameters L* (lightness), a* (red-green coordinate), b* (yellow-blue coordinate), C* (chroma) and h* (hue angle), together with the total color difference (ΔE*) all expressed relative to the corresponding mordant-free dyed reference. Color measurements were carried out using a Datacolor 110 LAV reflection spectrophotometer (Datacolor International, Lawrenceville, USA) with Tools II Plus software, under D65/10° illuminant/observer conditions.

3. RESULTS AND DISCUSSIONS

3.1. Visual appearance and distribution of CIELAB coordinates

The photographed textile series (Fig. 1) confirmed that *C. officinalis* generated a predominantly pale yellow to yellow-brown palette, while the mordant type altered the warmth, depth and greenish tendency of the final shade. Citric and tannic acid generally preserved lighter yellow-beige tones, whereas the systems containing $FeSO_4$ + oxalic acid and, to a lesser extent, $CuSO_4$ + oxalic acid shifted some samples toward darker beige, olive or greenish-yellow appearances.

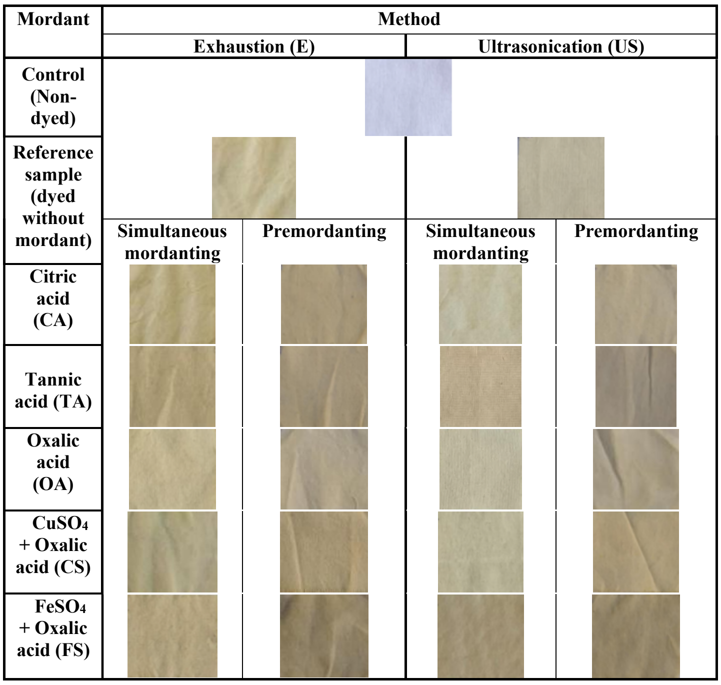

Fig. 1: *Representative appearance of the Calendula-dyed cotton samples obtained by exhaustion and ultrasonication procedure, after simultaneous mordanting and premordanting*

The CIELAB coordinate distribution (Fig. 2) supports the visual interpretation. Most experimental points remained in the positive Δb* region, showing that yellowness remained the dominant chromatic component after dyeing. Under simultaneous mordanting by exhaustion, citric and tannic acid produced positive Δa* and positive Δb* values, which are consistent with warmer yellow-orange hues. By contrast, simultaneous exhaustion with $CuSO_4$ + oxalic acid moved the sample into the negative Δa* domain (Δa* = -2.46), indicating a greener deviation. The most pronounced green shift was observed for premordanting followed by ultrasonication with $FeSO_4$ + oxalic acid (Δa* = -5.24; Δb* = 4.16), corresponding to an olive-like chromatic tendency. This behavior agrees with the literature showing that *C. officinalis* and related marigold-based dye systems usually maintain a yellow family of shades, whereas transition-metal mordants can darken the color and move it toward olive, brown, or greenish coordinates because of metal–dye complex formation [2,5,6,8].

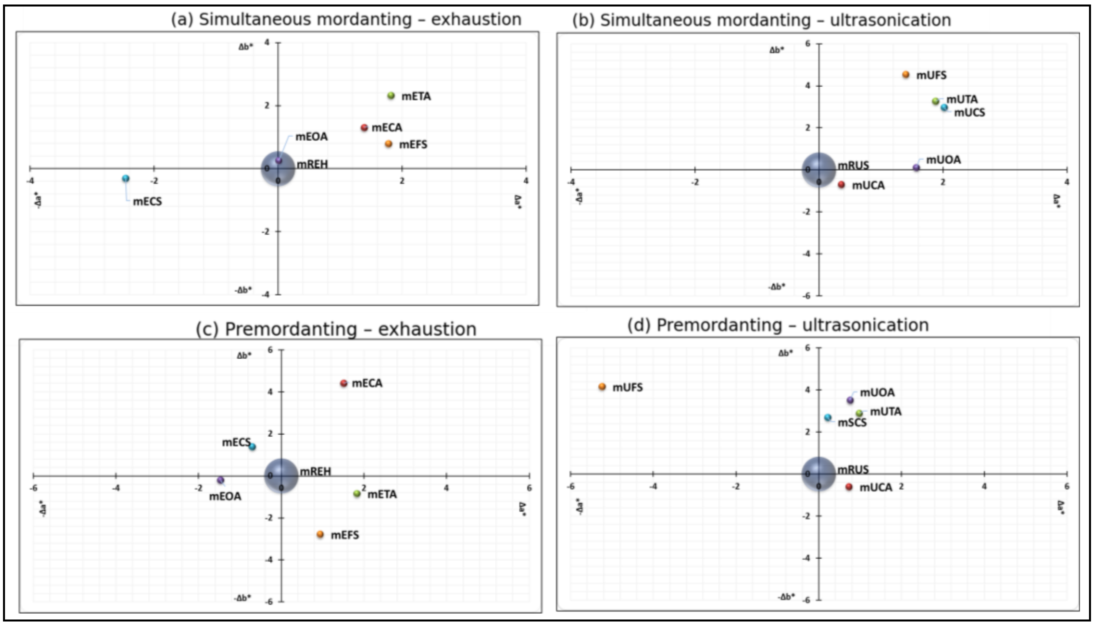

Fig. 2*: Distribution of Δa* and Δb* coordinates for Calendula-dyed cotton samples: (a) simultaneous mordanting–exhaustion; (b) simultaneous mordanting–ultrasonication; (c) premordanting–exhaustion; (d) premordanting–ultrasonication*

3.2. Effect of mordanting route and dyeing procedure on total color difference

The data in Tables 1 and 2 show that the mordanting route strongly influenced the overall color change. For the same mordant, premordanting generally increased ΔE* compared to simultaneous mordanting, especially under exhaustion. This trend was particularly evident for $FeSO_4$ + oxalic acid, for which ΔE* increased from 3.04 in simultaneous exhaustion to 7.54 in premordanting exhaustion. The same mordant also produced large deviations under ultrasonication (ΔE* = 5.74 for simultaneous mordanting and 6.72 for premordanting).

Within the simultaneous mordanting series, the smallest color modifications were recorded for oxalic acid in exhaustion (ΔE* = 1.73) and for citric acid in ultrasonication (ΔE* = 0.80), indicating shades closest to the reference. Therefore, these treatments may be preferred when subtle color adjustment is desired. By comparison, tannic acid under simultaneous ultrasonication (ΔE* = 4.10) and $FeSO_4$ + oxalic acid under the same method (ΔE* = 5.74) caused substantially stronger chromatic departures.

Table 1: *Colorimetric parameters and fastness values for cotton samples dyed with Calendula extract by simultaneous mordanting process*

Sample[1]	Dyeing method/ Mordant	ΔL*	ΔC*	ΔH*	ΔE*	Acid persp.	Alkali persp.	Dry rub.	Wet rub.
	Exhaustion								
mREH	**Reference**	82.61	24.55	90.15	-	2-3	3	3	2
mECA	10% Citric Acid	-1.11	1.33	-1.36	2.20	4-5	4	3-4	3
mETA	10% Tannic Acid	-2.22	2.38	-1.74	3.69	4	4-5	4	3-4
mEOA	10% Oxalic Acid	-1.71	0.25	-0.01	1.73	3-4	3-4	4-5	3
mECS	10% $CuSO_4$ + 10% Oxalic acid	-0.96	-0.19	2.47	2.66	5	4-5	4	3-4
mEFS	10% $FeSO_4$ + 10% Oxalic acid	-2.33	0.86	-1.76	3.04	4-5	4-5	4-5	3-4
	Ultrasonication								
mRUS	**Reference**	86.18	18.48	94.57	-	2-3	3	2-3	2
mUCA	10% Citric Acid	-0.15	-0.73	-0.31	0.80	4-5	4	3-4	3
mUTA	10% Tannic Acid	-1.60	3.21	-1.98	4.10	5	4-5	4-5	4
mUOA	10% Oxalic Acid	-2.09	0.05	-1.57	2.61	3-4	3-4	4	3
mUCS	10% $CuSO_4$ + 10% Oxalic acid	-1.52	2.92	-2.09	3.90	4-5	3-4	4-5	3-4
mUFS	10% $FeSO_4$ + 10% Oxalic acid	-3.21	4.49	-1.58	5.74	4-5	4	4-5	4

Table 2: *Colorimetric parameters and fastness values for cotton samples dyed with Calendula extract after premordanting procedure*

Sample[1]	Dyeing method/ Mordant	ΔL*	ΔC*	ΔH*	ΔE*	Acid persp.	Alkali persp.	Dry rub.	Wet rub.
	Exhaustion								
pREH	Reference	82.61	24.55	90.15	-	3	2-3	3-4	3
pECA	10% Citric Acid	-1.74	4.43	-1.43	4.97	4	3-4	4	3-4
pETA	10% Tannic Acid	-4.43	0.78	1.86	4.87	4	4	4-5	4
pEOA	10% Oxalic Acid	2.74	-0.13	1.48	3.11	3-4	3-4	4	4
pECS	10% $CuSO_4$ + 10% Oxalic acid	-3.48	1.41	0.66	3.81	4	4-5	5	4
pEFS	10% $FeSO_4$ + 10% Oxalic acid	-6.94	-2.77	-0.97	7.54	4-5	4-5	4-5	4
	Ultrasonication								
pRUS	Reference	86.18	18.48	94.57	-	2-3	2-3	3	2-3
pUCA	10% Citric Acid	-1.98	-0.59	-0.73	2.19	4	3-4	4	3-4
pUTA	10% Tannic Acid	-1.24	2.84	-1.12	3.30	4	4-5	4	4
pUOA	10% Oxalic Acid	-0.74	3.46	-0.94	3.66	3-4	3-4	4	3-4
pUCS	10% $CuSO_4$ + 10% Oxalic acid	-2.75	2.67	-0.39	3.86	4-5	3-4	4-5	4
pUFS	10% $FeSO_4$ + 10% Oxalic acid	0.68	-4.40	5.04	6.72	4-5	5	4	3-4

[1] **Sample code explanation:** the first lowercase letter indicates the mordanting strategy (**m** = simultaneous mordanting; **p** = premordanting). The following letter(s) indicate the dyeing method (**E** = exhaustion; **U** = ultrasonication), while the final letter(s) indicate the mordant type (**R** = reference sample dyed without mordant; **CA** = citric acid; **TA** = tannic acid; **OA** = oxalic acid; **CS** = $CuSO_4$ + oxalic acid; **FS** = $FeSO_4$ + oxalic acid).

In the premordanting series, exhaustion clearly intensified the effect of the mordants. Besides the strong action of $FeSO_4$ + oxalic acid, citric acid (ΔE^* = 4.97) and tannic acid (ΔE^* = 4.87) also increased the difference from the control more than in the simultaneous route. This suggests that pre-establishing the mordant on the fiber before dyeing can favor more pronounced *Calendula* fixation or altered complexation on the cellulosic support. Mechanistically, this sequential route may allow the mordant to interact first with hydroxyl groups on the cellulose surface and then act as an intermediate binding site for plant-derived chromophores, thereby increasing dye retention and modifying light absorption. Overall, citric acid behaved as the most conservative biomordant, whereas $FeSO_4$ + oxalic acid acted as the most powerful shade-modifying system.

A similar process dependence was reported by Mijas et al. for hemp/cotton fabrics dyed with *Calendula*, where the timing of mordant application significantly influenced color intensity and fastness [5]. More broadly, previous work on cotton shows that mordant sequence is not a minor technical detail, but a decisive variable because it determines how many coordination sites become available before the dye molecules reach the cellulose surface [3,9]. The fact that ultrasonication still generated appreciable ΔE^* values at only 40 °C is also consistent with reviews showing that ultrasonication can improve diffusion and dye transfer under milder processing conditions [7,10,11]. Nevertheless, in the present dataset, exhaustion plus premordanting generally remained the strongest combination for maximizing color change.

3.3. Color fastness to perspiration and rubbing

The fastness results indicate that *Calendula* dyeing can achieve moderate to good performance, particularly when mordants capable of stronger coordination are applied. For acidic perspiration, the highest rating (5) was reached by $CuSO_4$ + oxalic acid under simultaneous exhaustion and by tannic acid under simultaneous ultrasonication. Alkaline perspiration values were generally between 3.5 and 4.5, with the best result obtained for premordanting followed by ultrasonication with $FeSO_4$ + oxalic acid (grade 5).

Dry rubbing fastness of the colored samples was consistently higher than wet rubbing fastness for all investigated combinations, which is advantageous for practical handling and daily use. The best dry rubbing behavior was recorded for premordanting by exhaustion with $CuSO_4$ + oxalic acid (grade 5), while several other treatments reached 4.5, including tannic acid and $FeSO_4$ + oxalic acid systems. Wet rubbing was lower, but still acceptable in the best-performing samples, usually reaching grade 4. These trends confirm that part of the *Calendula*-derived color remains more vulnerable under wet mechanical action than in dry contact. Such a difference between dry and wet rubbing is commonly reported for natural-dyed cotton because loosely adsorbed surface colorants become more mobile in the presence of water [5,8,9].

From an application perspective, tannic acid appears to be the most balanced biomordant because it combined moderate-to-high chromatic enrichment with good perspiration fastness and comparatively strong rubbing resistance. This observation is in line with recent reviews describing tannin-based biomordants as particularly effective for cellulosic substrate due to their ability to improve dye adhesion while remaining more compatible with green textile processing than many conventional metallic salts [4]. At the same time, the metallic combinations with oxalic acid produced the strongest shades and generally the best durability, but at the price of a more pronounced departure from the reference yellow hue, which agrees with the broader literature showing that Fe- and Cu-based mordants often increase fixation and darken the final color [8,9]. $FeSO_4$- and $CuSO_4$-based mordanting should not be excluded from dyeing strategies, since these systems may offer important functional benefits, particularly improved dye fixation, deeper and more stable shades, and enhanced fastness performance. However, from a sustainability perspective, their use should be interpreted with an ecological caveat and rationally optimized for applications in which increased durability is required, while ensuring careful control of mordant concentration, fixation efficiency, and wastewater management. Therefore, the choice of mordant should be aligned with the desired end-use: subtle yellow shades with citric acid, balanced eco-performance with tannic acid, or darker olive-beige shades with enhanced fastness for $FeSO_4/CuSO_4$ systems.

4. CONCLUSIONS

The present study showed that *C. officinalis* petal extract can be successfully applied in the eco-dyeing of cotton fabrics through both exhaustion and ultrasonication. The dyed samples remained mainly in the yellow domain, but the final hue and intensity were strongly modulated by the mordant chemistry and by the application route.

Fastness properties to acidic and alkaline perspiration ranged from moderate to very good, and dry rubbing values were systematically superior to wet rubbing values. The best overall durability was obtained for $CuSO_4$ + oxalic acid and $FeSO_4$ + oxalic acid systems, while tannic acid emerged as a promising eco-friendlier alternative suitable for cotton products subjected to moderate use conditions.

The obtained results indicate that the appropriate selection of mordant type and dyeing route can significantly influence both chromatic expression and fastness performance. Biomordants such as citric and tannic acid maintained lighter yellow shades, while $FeSO_4$ and $CuSO_4$ combined with oxalic acid promoted darker olive-yellow tones and better fastness values, particularly under premordanting conditions. Overall, *C. officinalis* based dyeing offers a feasible route for developing aesthetically acceptable and functionally adequate cellulosic materials with potential hygienic or medical relevance. Further work should refine extract preparation, optimize fixation, and evaluate additional functional properties such as washing and light color stability, also possible antimicrobial activity.

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