



## Research article

## Surface functionalization of wool via microbial-transglutaminase and bentonite as bio-nano-mordant to achieve multi objective wool and improve dyeability with madder

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## ABSTRACT

Recently, natural dyes have a widening scope in various traditional and advanced applications due to their eco-friendly environment. However, improved dyeability of natural dyes still remains a challenging task. This research was aimed to achieve multi-objective wool with improved dyeability using bio-nano-mordant composed of m-Trans-glutaminase, m-TGase, and bentonite nanoclay. Wool fiber was treated through sonochemical method using different concentrations of m-TGase and bentonite. The surface morphology of wool fabric samples was examined by field emission-scanning electron microscopy (FESEM), and Fourier transform Infrared Radiation (FTIR). Further, wool samples treated at different conditions were applied to madder for dyeability examination. The optimum conditions of color coordinates, color strength, K/S, and washing fastness of madder on treated wool fabric with m-TGase and bentonite, were also examined. The results revealed well-made interactions among m-TGase, bentonite, and wool fibers. In addition, surface morphology was strongly influenced by variations in enzyme concentrations so that extra addition of m-TGase lead to clear damage scales or less cuticle surface in SEM images. Moreover, the results showed that the value of K/S for treated wool samples was better than untreated samples. Indeed, amongst all, 5% concentrations of bio-nano-mordant for m-TGase and bentonite have the most constructive K/S values. Similarly, results of  $\Delta E$  and antibacterial investigations also confirmed its superiority.

## 1. Introduction

Traditional chemical treatments and their usage have created environmental pollution as well as undesirable conditions in the textile industry which can cause undesirable side effects and serious health concerns in living beings. These issues could be overwhelmed and substituted with curative and constructive approaches. For example, in recent years, the uses of biotechnology and nanotechnology have gained significant recognition, not only because of the progressive way of altering textile fibers but also have eco-friendly characteristics [1, 2, 3, 4,

5, 6, 7, 8, 9]. The m-TGase bio-mordant [10, 11, 12, 13, 14, 15, 16] and nanoclay [17] are also the best candidates in the textile industry due to their favorable environmentally friendly properties. Furthermore, the lower toxicity of natural dyes as compared to the synthetic ones was clearly confirmed [1, 4, 18, 19]. Therefore, the research investigations have been in dire demand to look promptly for eco-friendly products produced from the natural resources [20, 21, 22, 23, 24].

Natural dyes are accomplished from natural resources (animals, plants, and minerals, etc.). They are biodegradable and non-toxic [18]. The fibers like silk, wool, and cotton have been dyed with natural dyes

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since ancient times [25]. However, these fibers do not have good affinity with natural dyes and thus show the poor to moderate washing and light fastness outcomes [26]. Consequently, conventional mordants (FeSO<sub>4</sub>, CuSO<sub>4</sub>, etc.) and eco-friendly mordants (bio-mordant, enzymes, etc.) have been applied during the dyeing process for better dye fixation and performance [4, 18, 27]. In the learning sources, several methods have been introduced to modify the surface of wool [28, 29] and other textile fibers i.e., hydrolysis by enzymes and reactants [30, 31, 32, 33, 34], and bonding with monomers [35], the usage of precarious CO<sub>2</sub> in scouring and dyeing [36], the microencapsulation of amalgamations, nimbus expulsion medication, gamma and UV treatment [32, 37, 38], ultrasonic vibrations [39], and plasma irradiation [33, 40]. However, all these approaches occasionally have caused physical, chemical and mechanical damages in fibers. An additional shortcoming of these kinds of techniques is the amelioration of producing on a large scale so that their utilization will be constrained for wet wool processing in textile manufacturing.

It is generally known that Madder, which is obtained from the root of *Rubia tinctorum* L., is produced in a variety of different colors ranging from orange to violet. Madder (CI Natural Red 9) is usually an evergreen plant up to 1.5 m high and has five yellow petals. The dye comes from its long roots and is composed of anthraquinones. Alizarin as the main coloring agent and purpurin are the most important components of Madder [41]. Many studies have been carried out for its application on textile fibers [34, 42, 43, 44, 45, 46].

With this perspective, herein dyeability of wool fabric is investigated with natural dye extracted from Madder by using pre-mordanting technique. Actually, m-TGase bio-mordant and bentonite nanoclay have been used to analyze their effects on the dye ability and influence on properties of wool. The aim of the present work is to examine the appropriateness of the Madder dye using bentonite and m-TGase as promising substitutes for mordant in the dyeing of wool with Madder.

## 2. Materials and methods

### 2.1. Materials

Scoured and un-dyed wool fabric with the size of 195 g/m<sup>2</sup> was purchased from Youngor Woolen Textile Company (China). Nonionic laundry detergent and standard washing soap (made of Chinese company) were used for scouring and washing fastness investigations. Acetic acid was obtained from a German company i.e. Merck, and utilized for pretreatment, dyeing, and after treatment processes. Bentonite nanoclay was procured from Aladdin (Bentone SD-2) with the chemical formula Al<sub>2</sub>O<sub>3</sub>·4(SiO<sub>2</sub>)·H<sub>2</sub>O. Transglutaminase (TG) was attained from Yiming Biological Products Co., Ltd. (Jiangsu, China). In addition, an Iranian Maddar roots powder was utilized as the natural dye.

### 2.2. Extraction process of dye

Firstly, the roots of Madder were purchased. A powder was prepared and dissolved in distilled water to form a solution. Secondly, the temperature of dye solution was raised up to the boiling point and retained in boiling for 60 min. Thirdly, the boiling was stopped and the temperature of the dye solution was cooled down to the room temperature and maintained for 24 h. Fourthly, filtration was carried out for the extraction of dye solution. Subsequently, the standard dye solution was prepared by adding distilled water to the filtered solution.

### 2.3. Enzymatic treatment

Three different concentrations i.e. 5%, 10%, 20% for m-TGase were selected. The liquor-to-goods ratio of enzyme to goods was L:G = 40:1 at 37 °C with the pH of 9–10. The samples were immersed for 5 min at 80 °C in an aqueous solution with pH: 5 that was adjusted by acetic acid. Thus

after the first treatment, the enzyme was kept inactivated in order to prevent hydrolyzing of wool.

### 2.4. Clay dispersions and wool treatment

To reduce the particle size and fully disperse the clay nano particles 3, 5, and 10% owf of clay particles were dispersed in an ultrasonic bath for 3 h with a liquor ratio of 50:1. Acetic acid was employed to adjust the pH of the dispersion solution (pH = 5) as a buffering solution. Then the wool fabrics were immersed in the solution under ultrasonic irradiation and maintained for 30 min in this condition. Finally, after washing by distilled water, squeezing and drying the samples were dyed with the madder powder.

### 2.5. Dyeing process

Prepared treated wool fabrics were dyed using the liquor of madder powder with the ratio of 50:1 for madder (50% owf) and acetic acid (5% v/v), respectively. The water bath shaker machine, DL-2003 (16), Suzhou Sidale Printing and Dyeing Machinery Co., Ltd., China, was used for the dyeing process, while keeping the bath temperature firstly at 40 °C. Then the temperature was increased to 80 °C in 20 min and continued for one hour. Briefly, the process was started with the treatment of wool by m-TGase (5%, 10%, 20% owf), followed by inactivation of the enzyme, then treatment with clay (at various concentrations of 3%, 5%, and 10% owf) and finally dyeing with madder (Figure 1).

## 3. Results and discussion

The untreated and treated wool fabric samples with bio-nano-mordant composed of m-TGase, and bentonite nanoclay were examined. Wool fibers were treated with different concentrations (5%, 10%, 20% owf) of m-TGase and (3%, 5%, and 10%) bentonite through sonochemical method. The influence on the surface morphology of wool fabric samples was studied through scanning electron microscopy (SEM). Further the optimum conditions of color coordinates, color strength, K/S, and washing fastness of madder on treated wool fabric with m-TGase and bentonite, were investigated. Figure 2 involved the whole process mechanism of the work analysis. All experiments were performed five times in order to achieve reliable data with the variation coefficient less than 5%. In fact, with the addition of an appropriate amount of m-TGase, the surface of wool was modified due to the occurrence of cross-linking reaction between

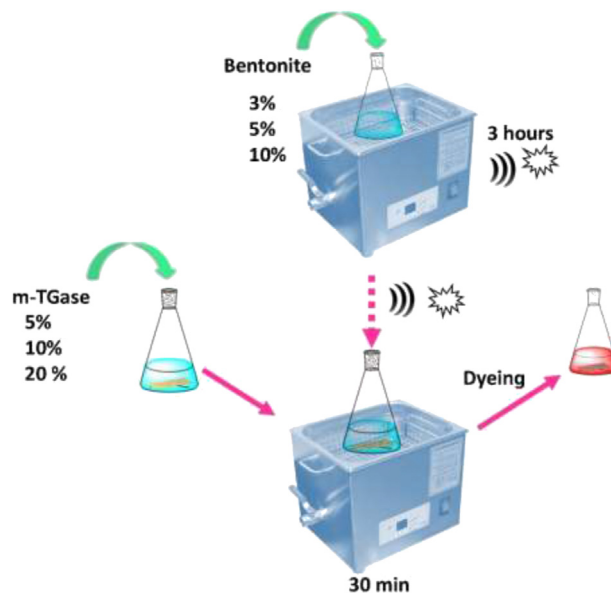


Figure 1. Schematic illustration of the wool treatment and dyeing process.

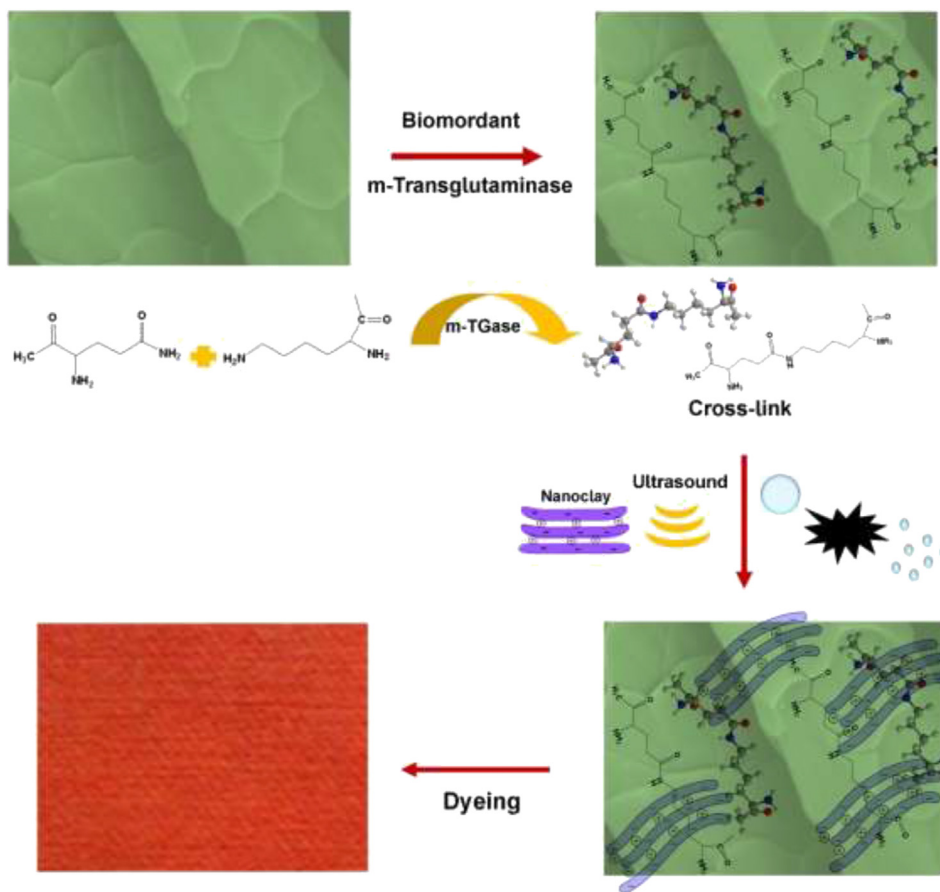


Figure 2. Schematic representation of proposed mechanism for treated wool by enzyme and bentonite.

glutamine and lysine, two main amino acids of wool. As-obtained inhomogeneous surface of wool with higher hydrophilicity [47] was interacted with hydrophilic bentonite and hence provided rough surface for the placement of dye molecules during the dyeing process.

3.1. Surface characterization

The SEM images of untreated and treated wool fabric samples were presented in Figure 3. The first image, Figure 3a, reveals a smooth surface of wool in the absence of bentonite and enzyme, while, rough surfaces

were observed when treated with bentonite and enzyme (Figure 3b-d). However, well dispersion and more distribution could be seen for the wool sample treated with m-TGase and bentonite (Figure 3d). Indeed, the SEM images indicated that the bentonite platelets were well dispersed and settled on the wool fiber surface after treatment of wool with m-TGase. In other words, after enzyme treatment, the wool fiber attained a lot of active places to interact with bentonite nanoclay and finally absorbed more dye molecules. EDS map analysis, FTIR and XRD investigations were also confirmed the presence of interaction (will discuss later).

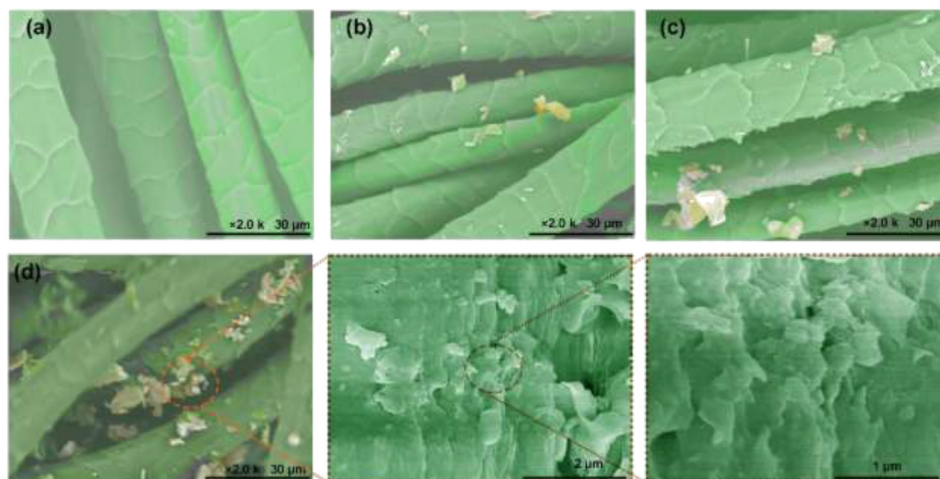


Figure 3. SEM images of untreated wool (a) and treated wool with m-TGase (b) bentonite (c), and m-TGase-bentonite at different magnification (d).

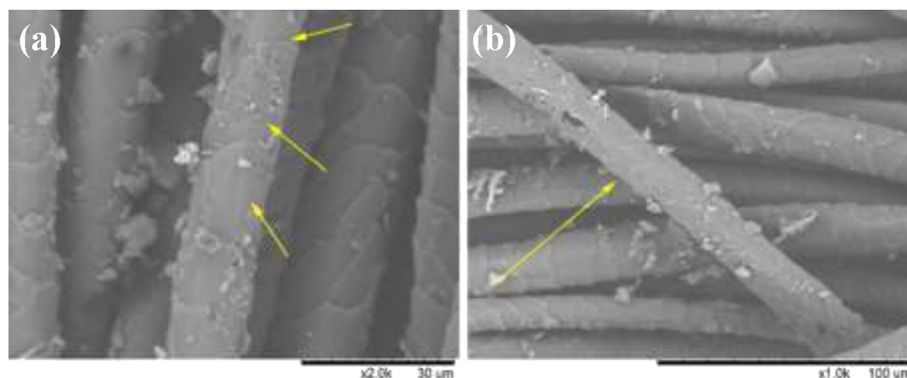


Figure 4. SEM images of treated wool with excess enzyme-clay (a, b at different magnifications).

Furthermore, various amounts of m-TGase (5%, 10% and 20%) and clay (3%, 5%, and 10%) were investigated to seek for the optimum conditions. Figure 4 displayed the SEM images that demonstrated the serious effect (destruction) on the surface of wool, caused by the addition of extra clay or enzyme. The scales of wool have been obliterated on the cuticle surface because of the alkali condition of enzymatic treatment. Thus, with the addition of excessive enzyme, more cross-link reaction occurred and extra alkaline condition was produced. Likewise, excessive clay caused the similar effect i.e., the particles aggregated on the wool without having any interactions and would be removed easily after dyeing and washing. Therefore, it is critical to add enzyme and bentonite

properly. It was observed that treatment of wool with the amount of 5% of m-TGase and 5% of bentonite caused the maximum dye absorption.

In order to get better information about the element distribution within the treated wool with enzyme and bentonite, energy dispersive X-ray spectroscopy (EDS) mapping was employed and the results provided in Figure 5. The presence of bentonite and enzyme on the surface of wool as well as the homogeneous distribution of the elements throughout the surface were confirmed. Actually, EDS analysis revealed distribution of Si and Al, representative of bentonite as well as C, O, S, and N as main elements of m-TGase. The presence of Pt element at the EDS spectra is related to the Pt coating before capturing SEM images.

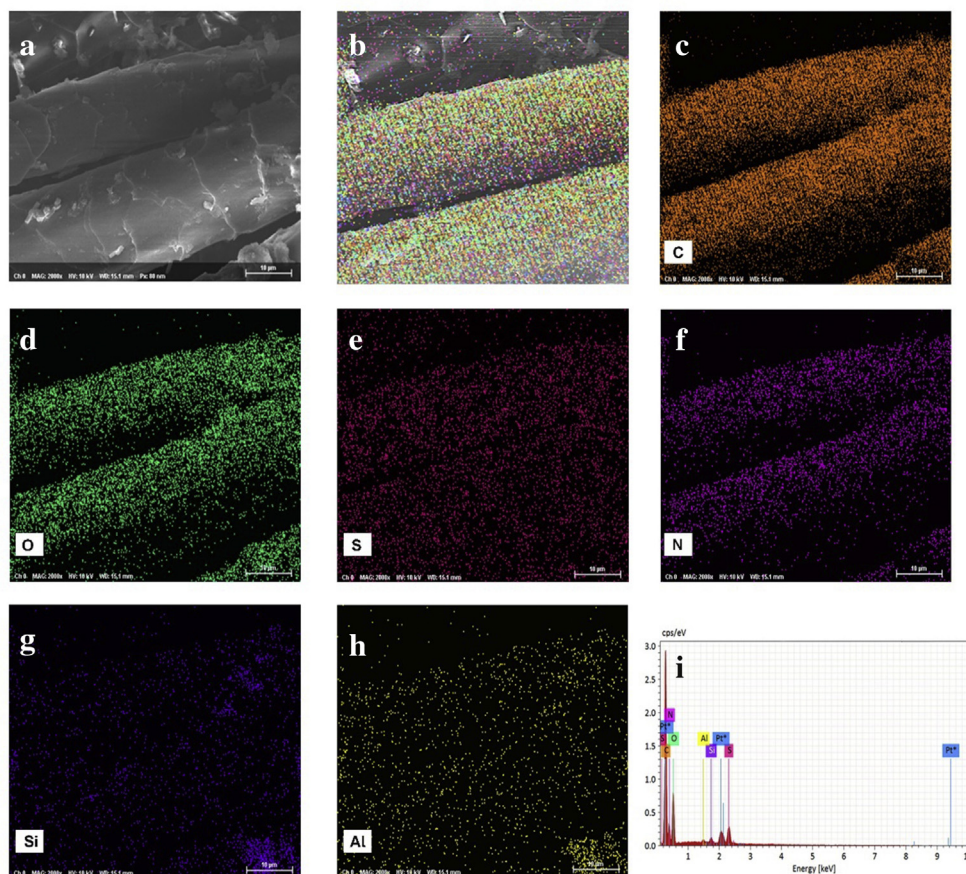


Figure 5. SEM (a), EDS elemental map (b–h), and EDS analysis data (i) of the surface for treated wool with m-TGase and bentonite.

### 3.2. Fourier transforms infrared spectroscopy (FTIR) analysis

The functional groups were characterized by FTIR; PerkinElmer Spectrum Two, USA in the range of  $4000\text{--}400\text{ cm}^{-1}$ . Figure 6 shows the FTIR spectrum of untreated and treated wool samples with enzyme, clay, and enzyme–clay. The spectra for the clay was displayed a characteristic peak at  $1040\text{ cm}^{-1}$ , related to the Si–O bond stretching, and doublet peaks at  $2800\text{--}2950\text{ cm}^{-1}$  arising from the C–H bond ( $\text{CH}_3$ ) within the clay structure and another doublet peak at  $500\text{--}600\text{ cm}^{-1}$  due to Si–O, Al–O and MgO bond bending [48]. The wool treated with bentonite and enzyme has the characteristic peaks in the spectrum as a consequence of their presence. However, a decrease in the peak intensity as well as shifting to the lower wavelength corresponded to the N–H (at  $3300\text{--}3600\text{ cm}^{-1}$ ) [49]. In details, amide band, arising from N–H stretching vibration coupled with –OH groups via hydrogen bonding [50], was observed at wave numbers of  $3270$  and  $3260\text{ cm}^{-1}$  for the wool sample treated with m-TGase and m-TGase/bentonite, respectively. The shift toward lower wavenumbers was observed when m-TGase was incorporated to bentonite.

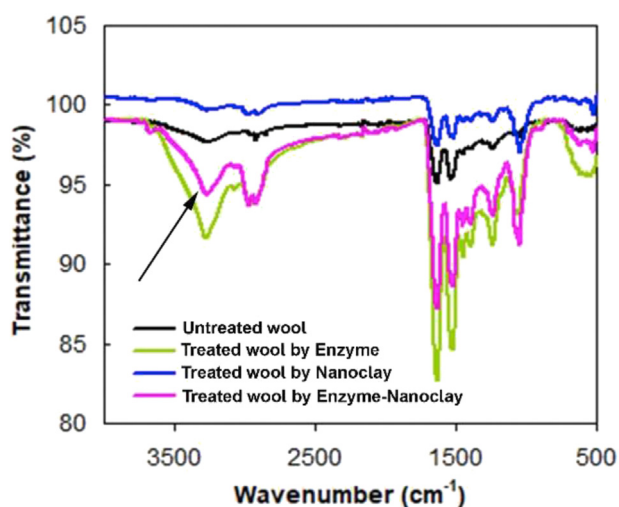


Figure 6. FTIR spectra of untreated and treated wool with enzyme, bentonite and enzyme-bentonite.

### 3.3. XRD analysis

Samples were further characterized using XRD (18KW Rotary Target X-ray Diffractometer). Figure 7 compares the XRD patterns of bentonite nanoclay, Wool-Clay, and Wool-Clay-Enzyme samples. The sharp diffraction peaks in XRD pattern of bentonite nanoclay shows the crystalline nature of nano-clay. Moreover, the crystalline peak at a  $2\theta$  value of

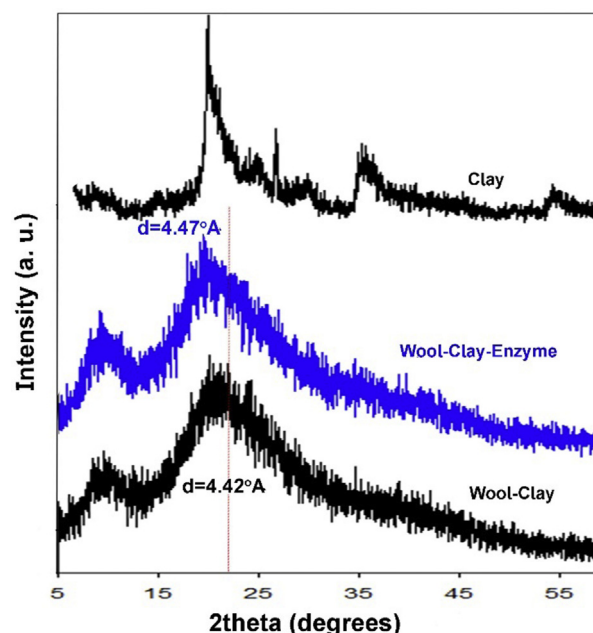


Figure 7. XRD patterns of Bentonite nanoclay, Wool-Clay, and Wool-Clay-Enzyme.

$\sim 20.06^\circ$  in Wool-Clay corresponded to the diffraction signal of the clay [51]. By closer look at the peak positions it would be observed that the peak was shifted to the lower  $2\theta$  value ( $\sim 19.84^\circ$ ) in Wool-Clay-Enzyme composite, indicating the intercalation of treated wool with m-TGase and bentonite. Besides, the  $d$ -spacing of clay, which was approximately at  $4.42^\circ\text{A}$  increased to the value of  $4.47^\circ\text{A}$  that confirmed the presence of intercalation [51, 52].

### 3.4. Anti-bacterial activity assessment

Wool samples treated with m-TGase and bentonite at various concentrations, were prepared and their anti-bacterial activity was investigated against *Staphylococcus aureus*, SA, as gram-positive bacteria and the results have been presented in Figure 8. For this, the method described in literature [53] was followed. The results indicated that with the addition of a suitable amount of m-TGase and bentonite, more anti-bacterial activities were observed.

### 3.5. Evaluation of color strength

Spectrophotometer (Spectra Flash-Data color SF-600) with illuminant D65 source, was employed to study the reflectance behavior of the fab-

Table 1. CIE  $L^*$   $a^*$   $b^*$   $C^*$   $h^*$  values of wool dyed with Madder using, m-TGase and Clay.

Compounds	Percentage (%)	$L^*$	$a^*$	$b^*$	$C^*$	$h^*$
Untreated	50	56.56	19.10	17.18	25.69	41.97
Enzyme 5%	Clay 3	39.66	27.95	26.13	38.26	43.07
	Clay 5	40.58	30.64	28.65	41.94	43.08
	Clay 10	42.34	29.16	26.43	39.36	42.20
Enzyme 10%	Clay 3	40.66	29.92	26.60	40.04	41.63
	Clay 5	40.73	29.50	26.80	39.85	42.26
	Clay 10	41.66	27.38	23.84	36.30	41.05
Enzyme 20%	Clay 3	41.87	27.51	22.82	35.75	39.67
	Clay 5	42.09	29.90	23.45	38.00	38.10
	Clay 10	43.94	28.96	22.18	36.48	37.44

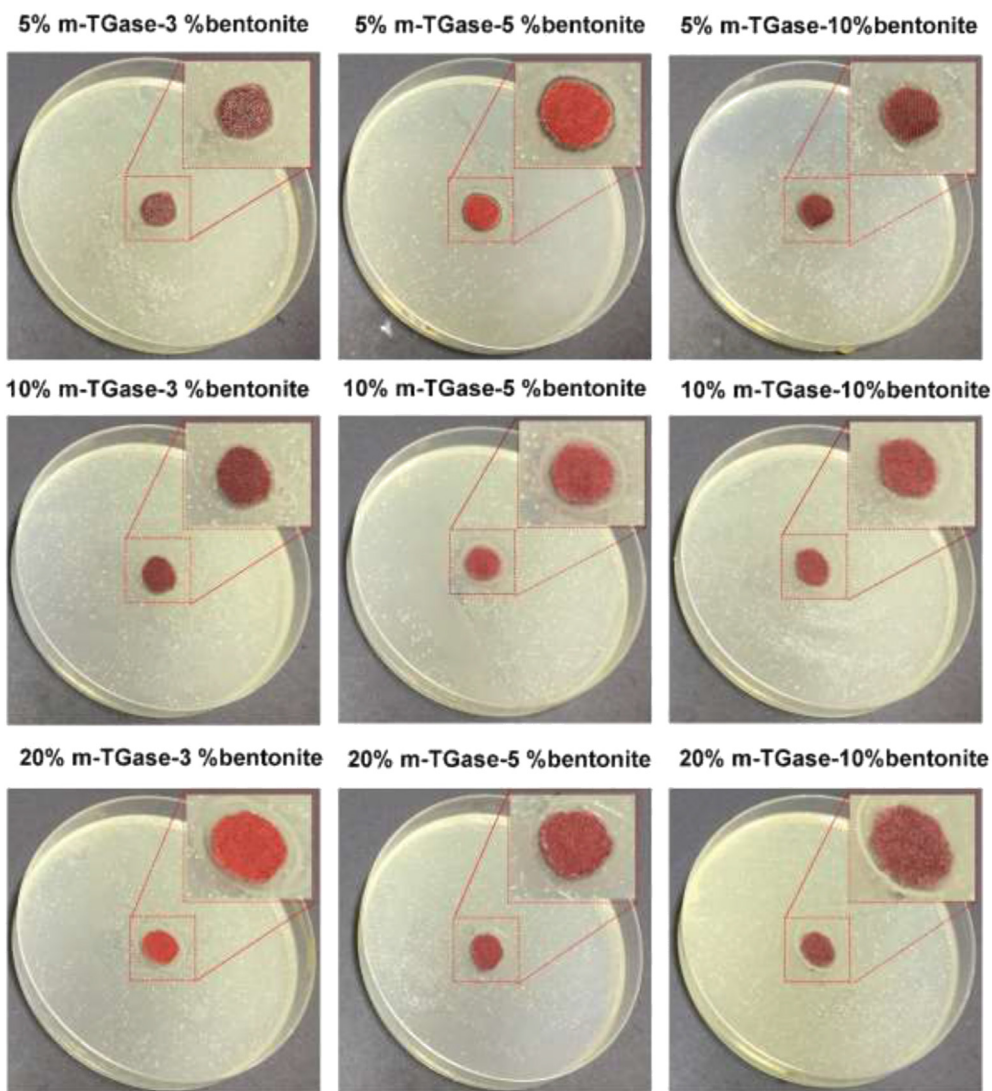


Figure 8. Comparative antibacterial activity of treated wool with different concentration of m-TGase and bentonite.

rics. The color strength (K/S) values were calculated using the following equation, Kubelka-Munk:

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

where K, S, and R are the absorption coefficient, scattering coefficient, and decimal fraction of the reflectance of the dyed samples, respectively.

Moreover, the color characteristics, well-known CIELAB color coordinates (L\*, a\*, b\*, C\*, h°) were measured for all of samples and the results were summarized in Table 1.

The light fastness of samples presented with the color coordinate of L\* measured the color of hue. By the decrease in light fastness values, there was an increase in the color absorption of the fiber. Furthermore a\* signified for the horizontal red–green color axis while b\* denoted the vertical yellow–blue axis.

In Table 1, it was observed that a\* and b\* values for the composition of 5 owf% of m-TGase and 5 owf% of bentonite was higher than others. It explained that prepared nano-bio mordant in these conditions showed more red (a\* = 30.64 as compared to 27.95 and 29.16) and yellow color (b\* = 28.65 as compared to 26.13 and 26.43). Furthermore, Figure 9 showed that maximum K/S was obtained for the treated wool sample with 5 owf% of m-TGase and 5 owf% of bentonite (green triangle).

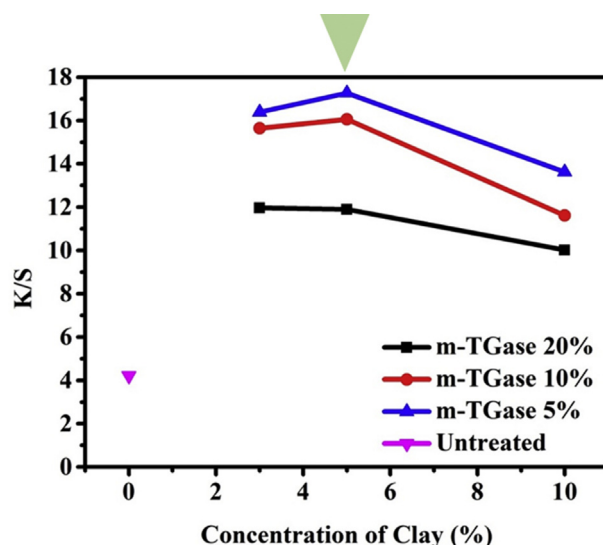


Figure 9. K/S values of wool dyed with Madder using, m-TGase and Clay.

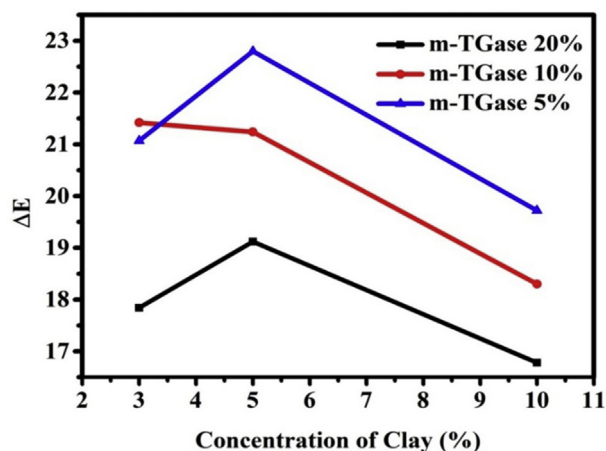


Figure 10. ΔE values of wool dyed with Madder using, m-TGase and Clay.

Alternatively, in order to quantify the evaluation of a concept that could only be described with adjectives, ΔE values were calculated and plotted in Figure 10. It is a useful parameter to investigate the properties of color as measuring the difference between two colors, which was a metric of interest in color science. Similarly, our results indicated that

optimum condition for prepared nano-bio mordant was 5 owf% of m-TGase and 5 owf% of bentonite.

It is well-known that m-TGase is a unique enzyme capable of catalyzing acyl transfer reactions by introducing covalent cross-links between glutamine and lysine in proteins and peptides [49, 54, 55]. Amino acids or alkyl ammonium ions act as a compatibilizing agents to treat clay structures since they exchange easily with ions between the silicates layers of clay [56]. Basically, nanoclay has anionic nature at neutral pH, and hence due to electrostatic repulsion, it is not interested in the adsorption of madder. Therefore, acetic acid was employed to adjust the pH under 7. In this way, OH<sub>2</sub><sup>+</sup> groups were created on the clay surface while acetate ions were associated with the outer surface of the clay [19]. During the dyeing process, the acetate ions were exchanged with dye ions, so that the electrostatic attraction was increased between the madder dye and OH<sub>2</sub><sup>+</sup> groups of clay. Meantime, the modified wool interacted with nanoclay through the ion exchange process. These interactions are summarized in Figure 11.

### 3.6. Analysis of color variation

The effect of bio-nano-mordant on color changes of woolen fabric dyed with madder was investigated and the results were shown in Figure 12. It was observed that the wool fabric treated with bio-nano-mordant changed the hue of the samples from pink to red. Alternatively, it was found that the color was changed to light red when the concentration of m-TGase increased.

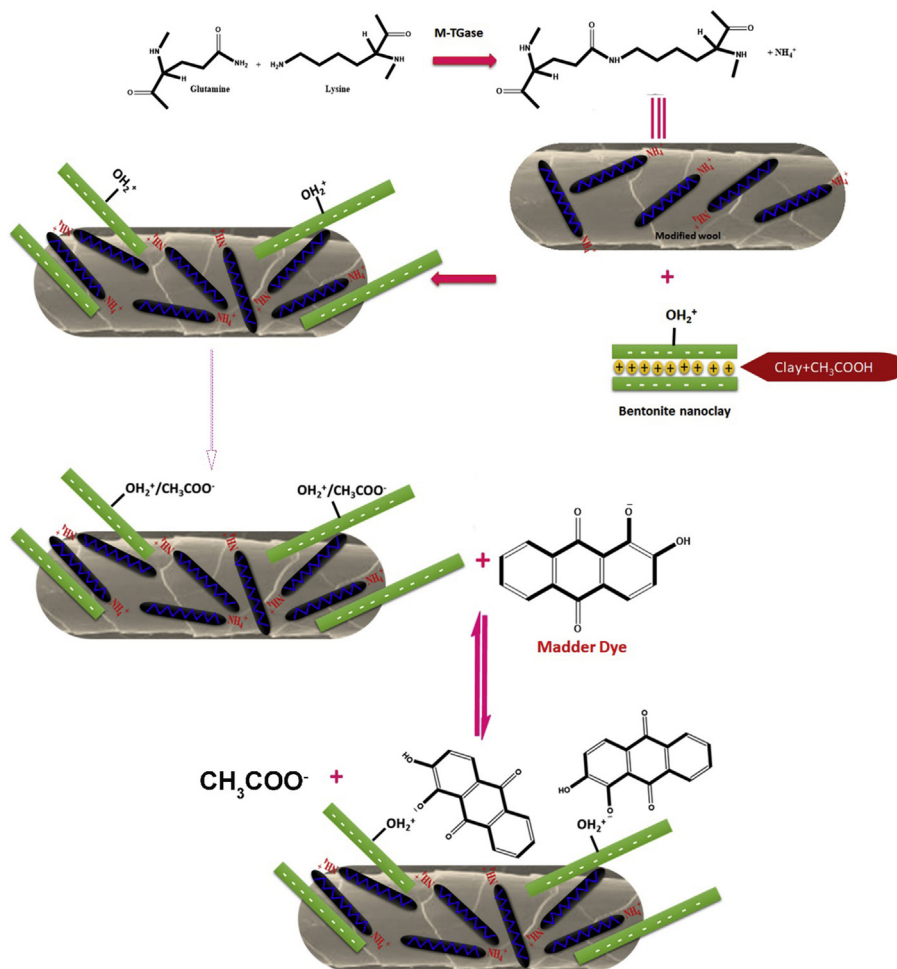
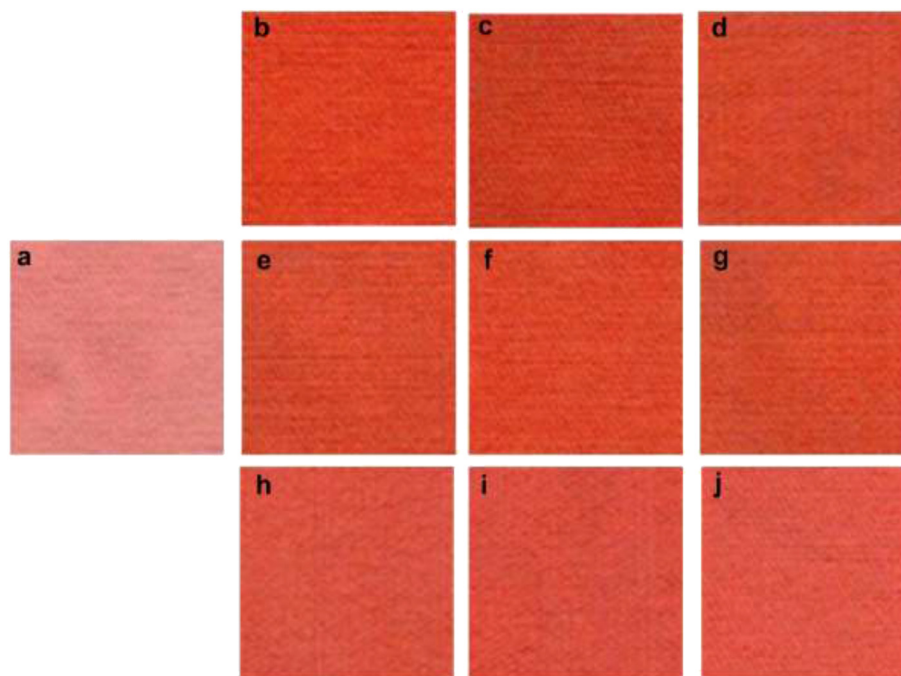


Figure 11. Chemical mechanism of involved reactions during the surface functionalization of wool via m-TGase and Bentonite to improve its dyeability with Madder.



**Figure 12.** Color of dyed wool: (a) untreated wool; treated wool with: (b) 5% m-TGase + 3% Clay, (c) 5% m-TGase + 5% Clay, (d) 5% m-TGase + 10% Clay, (e) 10% m-TGase + 3% Clay, (f) 10% m-TGase + 5% Clay, (g) 10% m-TGase + 10% Clay, (h) 20% m-TGase + 3% Clay, (i) 20% m-TGase + 5% Clay, and (j) 20% m-TGase + 10% Clay.

### 3.7. Determination of color fastness

The light fastness of the wool fabric samples was evaluated in the daylight according to ISO 105-B01 standard. With the help of blue scale, the assessment in the color variation (fading) was made. The fabric samples of wool were also evaluated for washing fastness through ISO 105-C01 standard. Grey scale was used for the assessment of variation in color (hue) and the degree of staining in the fabric samples after washing.

### 3.8. Light fastness

The most prominent properties of dyed garments are fastness. The variations of light fastness have been reported in Table 2.

### 3.9. Washing fastness

The washing fastness variation was measured using the grey scale and the results were reported in Table 3. Grey scale barometer was divided into 5 numbers i.e. the grade of 5 specified to zero contrast; conversely, 1

indicated the highest dye contrast. It was observed that the staining power of dyed and treated samples was suitable and no apparent variation was observed.

## 4. Conclusion

In conclusion, we have successfully achieved multi-objective wool and its improved dyeability with madder by surface functionalization of wool fabric samples with bio-nano-mordants composed of m-TGase and bentonite nanoclay at different concentrations. FTIR, SEM, color strength and antibacterial tests were also examined and compared. Results revealed that the surface morphology was greatly influenced by the variations in enzyme and bentonite concentration. Treatment of wool with 5% owf of m-TGase and 5% owf of bentonite promoted dyeability and absorbed more madder dye. Highest K/S and washing fastness values were obtained. Results of  $\Delta E$  and antibacterial performance were also observed superior as well.

**Table 2.** The influence on Light fastness of different compounds.

Compounds	Clay %	Light fastness
Untreated	-	2
Enzyme 5%	3	2–3
	5	2–3
	10	2–3
Enzyme 10%	3	2–3
	5	2–3
	10	2–3
Enzyme 20%	3	2–3
	5	2–3
	10	2–3

**Table 3.** The influence on washing fastness of different compounds.

Compound	Clay %	Wool	Cotton
Untreated	-	3	3–4
Enzyme 5%	3	3	3
	5	3–4	3–4
	10	3	3–4
	10	3	3–4
Enzyme 10%	3	3	3–4
	5	3–4	4
	10	3	3–4
	10	3	3–4
Enzyme 20%	3	3	3
	5	3	3
	10	3–4	4



## Declarations

### Author contribution statement

Reza Assefi Pour: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Robabeh Bagheri, Tayyab Naveed, Nadir Ali, Faisal Rehman: Contributed reagents, materials, analysis tools or data.

Jinxin He: Conceived and designed the experiments.

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### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

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