

Article

Surface Functionalization of Wool via Microbial-Transglutaminase as Bio-Mordant to Improve Dyeability with Madder in the Presence of Alum

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Abstract: Herein, the wool fabric was mordanted with alum, treated with microbial transglutaminase (m-TGase), and then dyed with madder. Different concentrations of alum and m-TGase were used to find out the optimum condition to achieve the best color after dyeing the wool fabrics with aqueous extract of madder. FT-IR spectroscopy and scanning electron microscopy (SEM) methods were applied to characterize the as-prepared samples. Contact angle measurements showed that the water uptake capability was increased in the case of the wool sample treated with alum and enzyme. Moreover, the samples were assessed for color strength (K/S) and color fastness. Our results showed that the optimal condition to get the highest color value was for the sample with 10% owf (of weight of fabric) alum and 5% owf m-TGase. Furthermore, it was found that there was a critical concentration for enzyme so that an increase in m-TGase amount would cause damage to the scales of fibers. The best condition of the dyeing process was discussed in this study, and also the proposed mechanism was presented. Indeed, treatment of wool with m-TGase led to a reduction in the amount of consumed alum, while investigations in color performances demonstrated the enhancement in color fastness, as well as color strength.

Keywords: mordant; natural dye; wool; microbial transglutaminase (m-TGase); madder

1. Introduction

Recent developments in dyeing and the requirements of the market encourage using natural dyes in the textile industry. Natural dyes have been attracting considerable attention to themselves due to their uncommon soft, lustrous, and soothing shades, which are pleasing to the human eye, being eco-friendly, producing a unique and harmonizing color, being renewable, and biodegradable [1–9]. Despite the mentioned advantages, there are some problems, such as limited access to natural dyes, low color efficiency, long dyeing time, low fastness, and costly mordanting process. Therefore, it is required to find a way to solve the difficulties of the dyeing industry.

To overcome these drawbacks, diverse techniques, such as cationization, plasma, enzyme, gamma, and microwave treatments, were employed for pretreatment of various textile fibers [4,10–20]. Fundamentally, the adhesion of natural dyes to natural fibers without any treatment, mordanting, or fixation is inferior [21–24]. Typically, mordants are metallic salts that can react with both dye and fiber. Indeed, mordants can act as a bridge, and by accepting an electron, they lead to the formation of coordination bonds with dye molecules. It is well known that by using mordant, the fastness of natural dyes, along with dye uptake, will be increased. Moreover, it is possible to obtain various

shades using only a single dye. There are some popular mordants, such as alum, copper, iron, chrome, and tin, which are widely used in the textile dyeing industry [22,25]. Alum is the most abundant metal salt in the earth, which is commonly used and considered as a safe mordant [26]. On the other hand, a cost-effective substitution way to produce natural colorants is ecological enzymatic natural dyeing [13,27–32]. Several studies have been reported on the enzymatic treatment of textile fibers to take advantage of their lower energy consumption and environmentally friendly processes in order to enhance dyeability, physical, and mechanical properties [23,33–40]. Microbial transglutaminase (m-TGase) is one of the TGase enzymes that has been considered for application in textile, wool, and leather processing due to the following special properties [41].

1. m-TGases can catalyze acyl transfer by forming covalent crosslinks between glutamine and lysine [15,42].
2. As m-TGase widely exists in hosts of different organisms and microorganisms, it can be produced at relatively low cost and the industrial level easily [41].
3. Since wool fibers are protein-rich fibers, m-TGase could be used to alter the characteristics of wool keratin [29,30,43–45].
4. It has been reported that m-TGase not only increases the strength of wool [40] but also improves the physical and mechanical properties [31,46–51], as well as washing fastness, and it also facilitates surface modification [30].

Although several studies have been done on using m-TGase in wool textile, the majority of them have been performed for the enhancement of mechanical properties. Therefore, employing m-TGase as eco-friendly processing in the dyeing process remains a key challenge in the pursuit of researches. The effect of m-TGase on dyeing properties of three natural dyes of curcumin, gardenia yellow, and lac [46], as well as sappan dye [29], have been investigated before.

From the discussions outlined above, it can be found that it is necessary to seek alternative methods to minimize the usage of dyes, mordants, and additives while retaining a desirable dyeing efficiency. Herein, we tried to reduce the amount of applied alum, as one of the most common mordants, with the help of enzymatic treatment. To do this, at first, the wool fabric was mordanted with different concentrations of alum, and then treated with m-TGase, and finally dyed with madder to improve the dyeability of wool through eco-friendly technique, as well as using less alum. Our findings brought a deeper understanding of the effect of wool treatment by alum to improve its dyeability with madder as a natural dye in the presence of m-TGase. Notably, to the best of our knowledge, there is no record in the literature for using alum and m-TGase to enhance the dyeability of wool with madder.

2. Experimental Work

2.1. Materials and Apparatuses

A woolen fabric (10 cm × 10 cm) with plain weave structure (195 g/m²) made by Youngor Woolen Textile Co., Ltd., Ningbo, China. Alum or Aluminum sulfate (K₂SO₄Al₂(SO₄)₃·24H₂O) was procured from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Microbial transglutaminase (m-TGase) was provided by Yiming Biological Products Co., Ltd., Jiangsu, China. Madder, which is known with the names of alizarine or the root of *Rubia tinctorum* L., is one of the ancient natural dyes and produces the colors ranging from orange to violet. This color was prepared from the aqueous extract obtained from the powdered roots of Iranian madder grown in Yazd. It is an old and famous plant widely used in the Iranian carpet industry. Standard washing soap and standard synthetic detergent were purchased from Shanghai White Cat Chemicals Co., Ltd., Shanghai, China. Acetic acid was supplied by Merck, Darmstadt, Germany.

The surface morphology of the samples was observed by using SEM, Hitachi TM-1000, Tokyo, Japan. FTIR (PerkinElmer Spectrum Two, Waltham, MA, USA, in the range of 4000–400 cm^{−1} at a resolution of 4 cm^{−1}) spectrometer was used to examine the chemical composition of the woolen fabric.

Also, DSA30 (Kruss, Germany) water contact angle-meter was employed to measure the contact angle of the samples. The deionized water was used with a volume of 5 μL in one drop.

2.2. Dye Extraction

The madder powder was obtained from madder root. Then, the required amount of natural dye powder was dissolved in water along with continuous stirring at 100 $^{\circ}\text{C}$ for 1 h. The solution was maintained at room temperature for 24 h. Finally, the dye solution was filtered and then diluted with the addition of distilled water to the standard dye solution.

2.3. Mordanting, Pretreatment of Wool with Enzymes, and Dyeing Procedures

The conventional method of mordanting was performed on the wool fabric by using alum. The woolen fabric was immersed in 5%, 10%, and 20% owf of the alum solution at a liquor ratio of 40:1. The pH of the bath was adjusted at 4 using acetic acid. The bath temperature was increased from 40 $^{\circ}\text{C}$ to boiling point over 20 min and was maintained at this temperature for 1 h. Afterward, the woolen fabric was washed with water and finally dried. In the next step, the wool fabric was treated with three different concentrations of m-TGase, 5%, 10%, and 20% w/w, at a liquor to fabric ratio of 40:1 in the pH of 9–10 and at 37 $^{\circ}\text{C}$ for one hour. The enzymes were inactivated in a solution with pH 5, while it was adjusted using acetic acid for 5 min at 80 $^{\circ}\text{C}$, and then it was washed with water to prevent the hydrolyzation of wool. Finally, the mordanted fabrics with alum and enzyme were dyed with the madder (50% owf) and acetic acid (5% v/v) at a liquor ratio of 50:1 in the water bath shaker machine (DL-2003 (16), Suzhou Sidale Printing and Dyeing Machinery Co., Ltd., Suzhou, China). The dyeing bath temperature was set from the starting point of 40 $^{\circ}\text{C}$ to 80 $^{\circ}\text{C}$ in an over 20 min period and was further continued for 60 min.

3. Results

3.1. FT-IR Analysis

FT-IR spectra of untreated wool and treated wool with alum, m-TGase, and alum-m-TGase are presented in Figure 1. A closer look at the spectrum of untreated wool fibers showed divers distinguished absorption peaks, including a broad peak in 3500–3100 cm^{-1} and several peaks at about 1612, 1506, and 1216 cm^{-1} . The first broad one could be assigned to the –NH-stretching vibration, while the other three peaks were related to amide-I, amide-II, and –C–N stretching of amide-III, respectively [52,53]. All characteristics peaks of wool fiber, alum, and m-TGase were found in the treated wool with alum and m-TGase samples with a little bit lower intensity as compared to the wool-enzyme sample (gray circles). The lower intensity of peaks indicates the entanglement of amine groups in the interaction between wool-enzyme, alum, and dye molecules [54].

In treated wool with alum spectrum, the band centered at about 1040 cm^{-1} belonged to sulfate absorptions. The sulfate peak appeared after modification of wool with alum, as well as alum and m-TGase. Further, the broad absorption band located at about 500–600 cm^{-1} probably was because of the combined absorptions of sulfate, and the Al–O stretching vibrations. It should be noticed that in the spectrum of treated wool with m-TGase, there was a peak at about 1020–1250 cm^{-1} , which was related to C–N stretch (aliphatic amines). The intensity of this peak was increased in the FT-IR spectrum of the wool sample treated with alum and m-TGase, indicating the effect of both alum and enzyme. The bands between 2750 cm^{-1} and 3000 cm^{-1} are related to stretching vibrations of C–H bonds in –CH₂ [55].

Moreover, it could be found that the intensity of observed peak at about 500–600 cm^{-1} , which was due to metal–O bond bending, was decreased in the wool-alum-enzyme sample as compared to wool-enzyme. This behavior could be assigned to the interaction between Al from alum and specific functional groups present in the madder [56]. In order to further investigate the above-discussed results, the FT-IR spectra of the samples treated with different concentrations of m-TGase and alum

were recorded, and the results confirmed that by increasing the alum concentrations, the intensity of the mentioned peaks was decreased, demonstrating the involvement of amine group in the interaction between wool, alum, and madder [57].

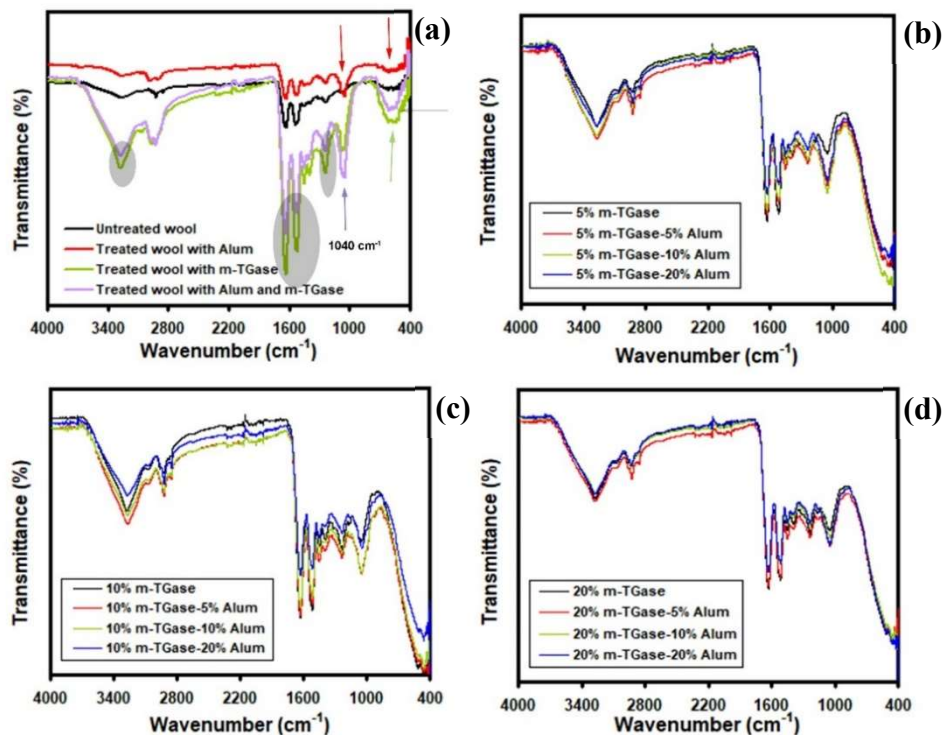
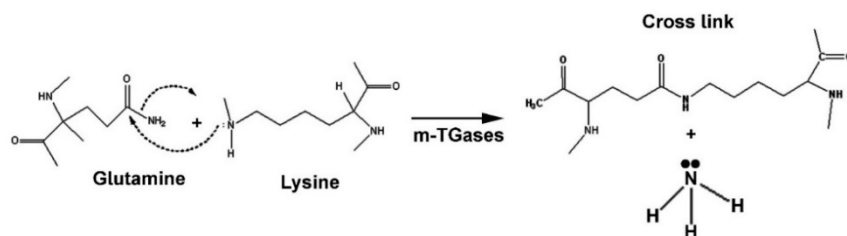


Figure 1. FT-IR spectra of (a) untreated and treated wool with microbial transglutaminase (m-TGase), alum, and alum-m-TGase; Treated wool with (b) 5%; (c) 10%; (d) 20% m-TGase with various concentrations of alum.

3.2. Surface Morphology

The surface changes of wool fibers treated with various concentrations of m-TGase and alum were investigated, and the SEM images are presented in Figure 2a–c. Our results showed that by increasing m-TGase concentration, some surface damages appeared so that some of the scales were damaged and led to less cuticle surface (Figure 2b). This phenomenon probably was because of alkali condition, which is obtained as a result of more cross-link reaction by adding more m-TGase [43]. Indeed, m-TGase affected wool fiber by following cross-link reaction between glutamine and lysine, which are present in wool structure:



Therefore, it is essential to use the enzyme in a suitable amount.

Moreover, energy dispersive X-ray spectroscopy (EDS) mapping provided more and better information about the elemental distribution on the surface of treated wool. The presence of Al as a representative of alum along with C, S, N, and O as main elements of m-TGase confirmed the modification of wool fibers with both alum and enzyme (Figure 3). Besides, the homogeneous distribution of the elements throughout the surface was confirmed.

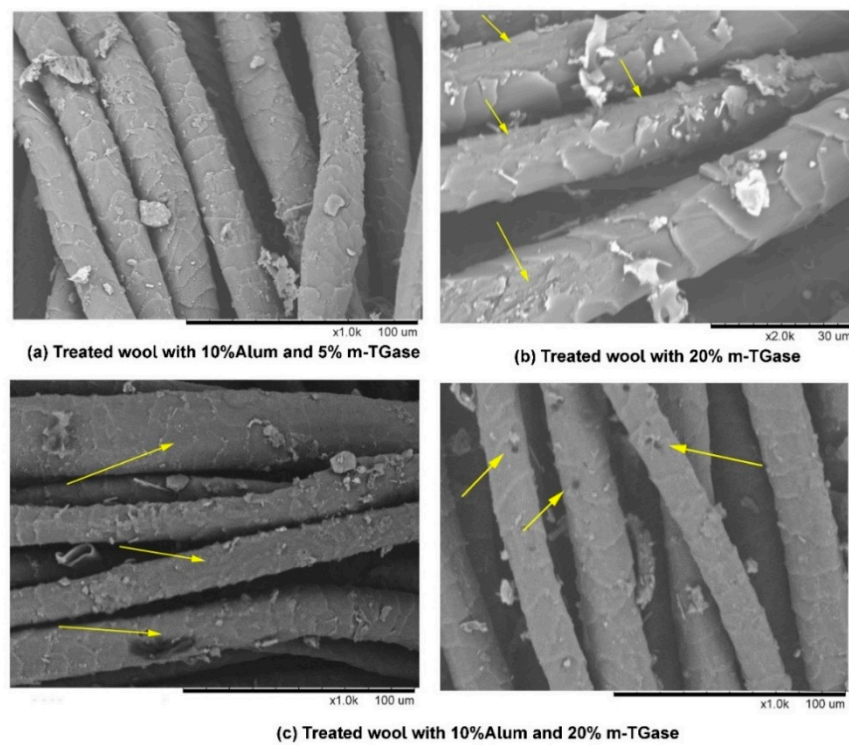


Figure 2. SEM images of treated wool with (a) 10% alum-5% m-TGase, (b) 20% m-TGase, and (c) 10% alum-20% m-TGase; using more m-TGase caused surface damages on wool fiber.

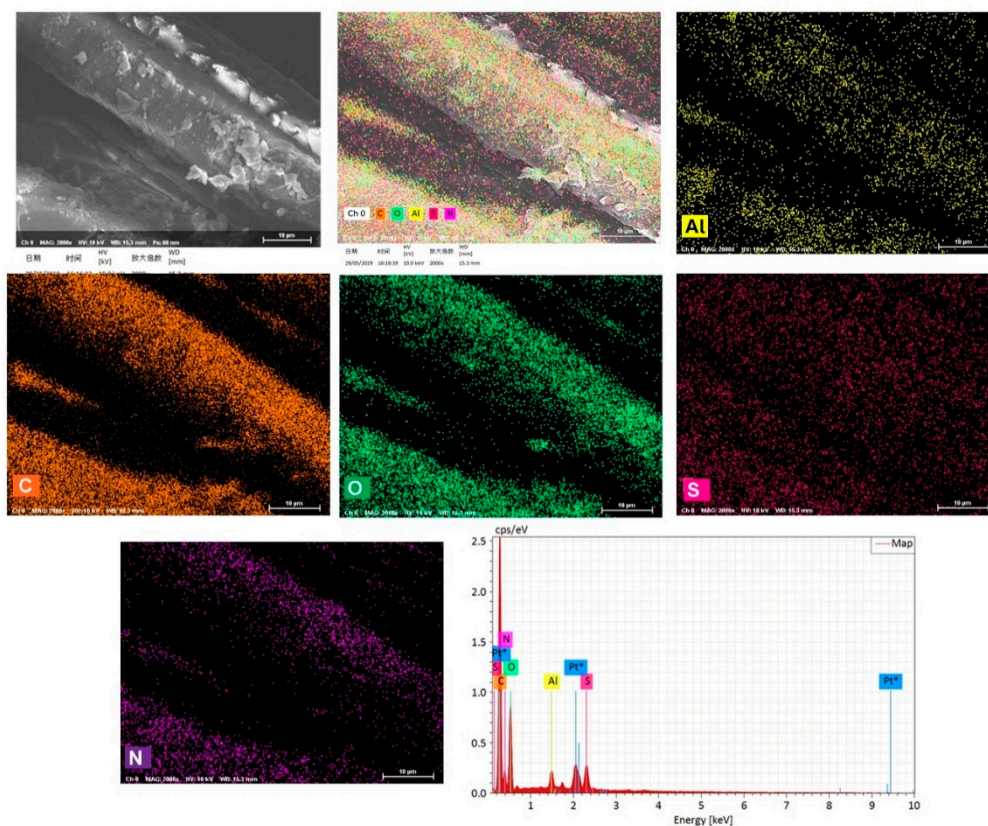


Figure 3. EDS elemental map of the surface for treated wool with alum and m-TGase.

3.3. Contact Angle and Wettability

The water contact angle on different samples was measured, and the results are presented in Figure 4. As could be seen, the water contact angle was decreased on the wool sample treated with 10% alum and 5% m-TGase, indicating the enhancement of hydrophilicity of treated wool fiber. It seemed that the surface functionalization of wool with alum and m-TGase led to an increase in roughness and, hence, improvement of dyeability of wool with madder.

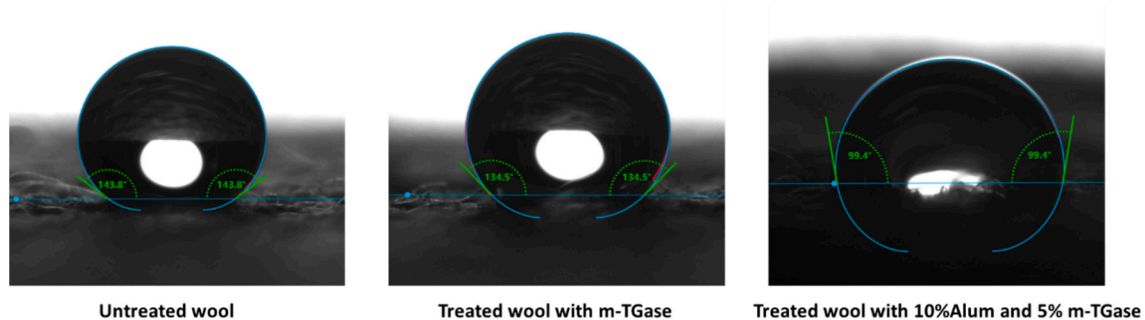


Figure 4. Water droplets on untreated wool; treated wool with 5% m-TGase; treated wool with 10% alum and 5% m-TGase.

3.4. Colorimetric Analysis

The spectra flash-data color (SF-600) was used with a spectrophotometer to check the color properties of colored specimens. The correlation of the CIELAB color (L^* , a^* , b^* , C^* , h°) was measured for each sample in the D65 light source with a standard observer of 10 degrees. The light reflection method was used to calculate the color value (K/S) of the samples using the following equation:

$$K/S = (1 - R)^2/2R \quad (1)$$

where K is the absorbance coefficient; S is the coefficient of scattering, and R is reflectance percentage. Table 1 shows the effects of alum and m-TGase concentrations on the colorimetric properties of the mordanted wool fibers.

Table 1. Colorimetric properties of wool fibers dyed with madder treated with alum and m-TGase at different conditions.

	%	L^*	a^*	b^*	C	h	K/S
Untreated	-	56.56 ± 1.27	19.10 ± 0.57	17.18 ± 0.97	25.69 ± 0.81	41.97 ± 0.48	4.21 ± 1.32
Alum	5	40.10 ± 1.46	40.47 ± 0.76	27.35 ± 0.82	48.85 ± 0.45	34.05 ± 0.49	14.83 ± 1.40
	10	37.50 ± 1.45	38.18 ± 1.28	26.92 ± 0.96	46.71 ± 0.61	35.19 ± 1.41	17.81 ± 1.00
	20	37.24 ± 1.14	40.99 ± 1.05	26.44 ± 1.31	48.78 ± 0.85	32.82 ± 1.06	16.73 ± 0.89
	20	37.24 ± 1.14	40.99 ± 1.05	26.44 ± 1.31	48.78 ± 0.85	32.82 ± 1.06	16.73 ± 0.89
Enzyme	5	40.72 ± 2.10	28.46 ± 0.79	24.76 ± 1.82	37.72 ± 1.32	41.03 ± 1.34	14.14 ± 1.04
	10	40.01 ± 1.22	31.84 ± 1.38	26.96 ± 1.17	41.73 ± 1.41	40.25 ± 1.47	16.34 ± 1.05
	20	39.79 ± 2.03	30.45 ± 0.96	25.89 ± 1.70	39.96 ± 0.79	40.37 ± 1.08	16.25 ± 0.86
Enzyme 5%	Alum 5	37.67 ± 1.12	39.73 ± 1.18	29.63 ± 0.83	49.56 ± 0.67	36.72 ± 1.72	20.33 ± 0.98
	Alum 10	35.67 ± 1.26	39.53 ± 1.39	28.62 ± 0.85	48.81 ± 1.07	35.91 ± 1.22	21.55 ± 0.82
	Alum 20	36.98 ± 1.22	42.25 ± 1.29	29.12 ± 1.63	51.31 ± 0.98	34.58 ± 1.55	20.54 ± 1.32
Enzyme 10%	Alum 5	37.81 ± 1.63	39.30 ± 0.62	27.05 ± 1.05	47.71 ± 0.90	34.53 ± 1.26	17.26 ± 1.12
	Alum 10	39.43 ± 1.26	39.28 ± 1.10	29.52 ± 1.23	49.13 ± 1.00	36.93 ± 0.81	17.42 ± 1.04
	Alum 20	38.14 ± 1.25	40.53 ± 1.12	29.86 ± 0.88	50.34 ± 1.25	36.37 ± 0.77	19.74 ± 1.01
Enzyme 20%	Alum 5	37.86 ± 1.75	37.20 ± 1.33	26.58 ± 0.63	45.72 ± 0.88	35.54 ± 1.52	17.35 ± 0.90
	Alum 10	38.63 ± 2.51	38.38 ± 2.06	28.65 ± 1.10	47.90 ± 0.84	36.74 ± 0.52	18.14 ± 0.96
	Alum 20	34.81 ± 2.16	38.96 ± 5.19	26.63 ± 0.79	47.20 ± 0.60	34.35 ± 0.85	21.54 ± 1.31

By taking a closer look at the data, it could be found that the values of lightness (L^*) for all treated samples were less than untreated wool fabric, indicating better absorption of color in the treated samples. Likewise, (a^*) values were increased, demonstrating an increase in the color red. The a^* and b^* values of dyed samples treated with alum and m-TGase indicated that all the samples were found in the red-yellow zone.

The effect of different concentrations of mordants on the color strength (K/S) is illustrated in Figure 5a. It showed that the K/S of the wool fabric treated with 10% alum and 5% m-TGase and dyed with madder was the best as compared to others. In agreement with previous results, it could be found that using more m-TGase not only does not improve the color strength, but it could also have the opposite effect. Also, it was observed that by increasing alum concentration to 20%, the color strength was decreased (pink). It might be assigned to the fact that by increasing alum concentration, the surface of wool would be covered, and there would be few available places, which can be affected by m-TGase. Therefore, using a 10% alum along with 5% m-TGase led to the maximum color strength.

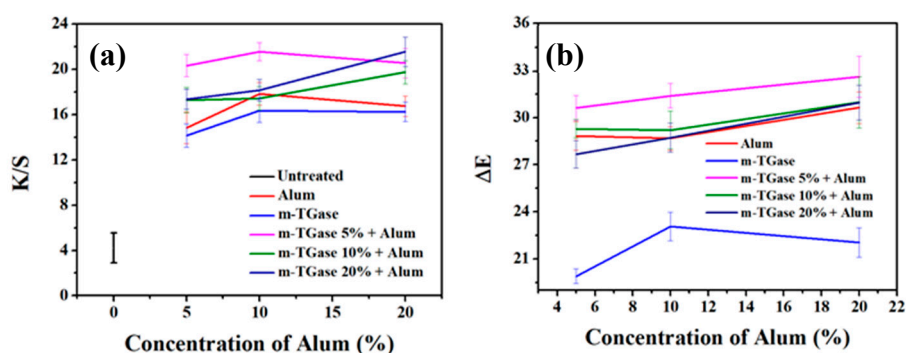


Figure 5. (a) Color strength and (b) Color difference (ΔE) of untreated and treated wool.

Further, the total color difference was obtained using Equation (2):

















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

where $\Delta L = L^* \text{ sample} - L^* \text{ standard}$; $\Delta a^* = a^* \text{ sample} - a^* \text{ standard}$; $\Delta b^* = b^* \text{ sample} - b^* \text{ standard}$ (ASTM Standards, D2244–11, 2011). Figure 5b elaborates on the ΔE results of the treated wool samples with alum and m-TGase with different concentrations. As expected, the color difference (ΔE) for wool fabric dyed with madder accompanied by alum and 5% m-TGase showed the maximum values.

3.5. Color Variation

The effect of m-TGase and alum on the appearance of the wool dyed with madder is shown in Table 2. The results showed that wool treated with alum and m-TGase changed the hue of the samples from pink to a lovely red. It was observed that with increasing m-TGase with different concentrations of alum, the hue of the samples was changed to dark red.

Table 2. Color of dyed wool (treated and untreated).

Untreated	Treated		
	Alum 5%	Alum 10%	Alum 20%
			
	m-TGase 5%	m-TGase 10%	m-TGase 20%
			
	m-TGase 5% + Alum 5%	m-TGase 5% + Alum 10%	m-TGase 5% + Alum 20%
			
	m-TGase 10% + Alum 5%	m-TGase 10% + Alum 10%	m-TGase 10% + Alum 20%
			
	m-TGase 20% + Alum 5%	m-TGase 20% + Alum 10%	m-TGase 20% + Alum 20%
			

3.6. Color Fastness Performance of Dyed Woolen Samples

Table 3 shows the light fastness, as well as washing fastness results. The results of color fastness were based on the scale of blue wool (1–8), in which grade 1 means very poor, and grade 5 is excellent. Obviously, it could be seen that the light fastness of the treated samples was more than the untreated sample.

The properties of the washing fastness of the stained samples were measured according to the ISO standard, which is a period equal to five general wash periods. According to grayscale, increasing washing fastness for all samples was observed compared to the untreated one. It should be noticed that although using alum along with enzyme brought about reduced washing fastness values for cotton, but other obtained results demonstrated that the amount of used alum was decreased as compared to other reported dyeing methods [58,59]. Indeed, any reduction in alum amount would be useful as it is a very common mordant in the carpet industry on one side and is harmful to the environment as well as people. Therefore, this work was focused on reducing the amount of used alum by employing m-TGase, and the obtained results showed that using 10% alum and 5% m-TGase would lead to high efficiency in dyeing performance.

Table 3. Variation of color fastness under different treatments.

	%	Light Fastness	Wash Fastness	
			Wool	Cotton
Madder	50	2	3	3–4
Alum	5	3–4	4–5	5
	10	3–4	4–5	5
	20	3–4	4–5	5
Enzyme	5	2–3	3–4	4
	10	2–3	4	4–5
	20	2–3	3–4	4
Enzyme 5%	Alum 5	3–4	4–5	4–5
	Alum 10	3–4	4–5	4–5
	Alum 20	3–4	4–5	4–5
Enzyme 10%	Alum 5	3–4	4–5	4–5
	Alum 10	3–4	4–5	4–5
	Alum 20	3–4	4–5	4–5
Enzyme 20%	Alum 5	3–4	4–5	4–5
	Alum 10	3–4	4–5	4–5
	Alum 20	4	4–5	4–5

4. Discussion

Our goal is to reduce the amount of consumed alum due to its health and environmental problems. Results showed that by applying a certain amount of m-TGase, this target could be attained by using less alum to achieve the desired dyeing efficiency. Characterization data confirmed that treating of wool with alum and m-TGase would cause some effects on wool fibers: At first by adding alum as mordant, it would be attached to the fiber molecules of wool, and, on the other hand, by treating of wool with m-TGase, cross-link reaction occurred between two amino acids of wool. As a result of using m-TGase, up and down places were created, especially in the place of scales. The proposed mechanism was that first aluminum sulfate mordant anchored to the fiber, and then by treating with m-TGase, morphological changes were obtained in the wool fibers. Following which, the anchored alum chemically combined with certain functional groups present in the madder, while the as-generated rough surface provided the suitable places for trapping the madder molecules. Thus, the combination of both physical and chemical effects improved the dyeing efficiency in the present work. The schematic illustration for the proposed mechanism is presented in Figure 6.

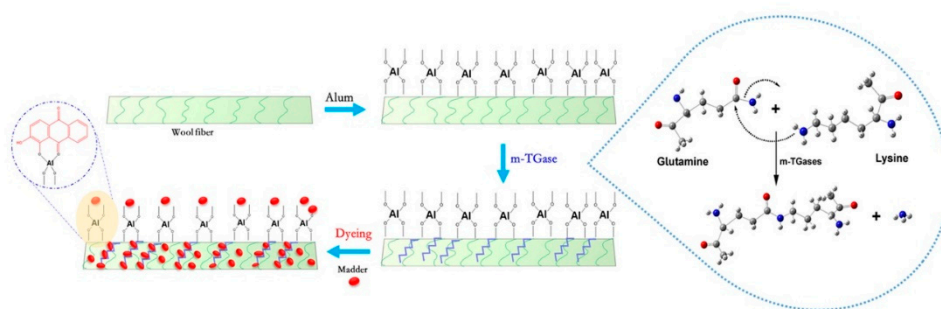


Figure 6. The schematic illustration for the proposed mechanism of treated wool with alum and m-TGase.

5. Conclusions

In summary, to extend an effective and robust dyeing system for madder as a widely used natural color, treatment by alum, along with enzymatic modification of wool, was employed. Toward the attainment of optimum preparation conditions, different concentrations of alum and enzyme were tested. FT-IR analysis and SEM characterization results confirmed the presence of interaction between alum, m-TGase, and wool fibers. Also, it was found that to achieve the most beneficial dyeing system for madder through using alum and m-TGase, it was necessary to prepare the coatings with exact concentration. The color strength (K/S) and color coordinates also were calculated for all samples prepared at different concentrations. By considering all obtained results, it was found that the optimum condition for preparing a new dyeing system for madder on wool fibers was using 10% owf alum and 5% owf m-TGase.

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