

## Evaluation of the dyeing and fastness properties of wool fabrics treated by chitosan in different molecular weights and dyed with mint

### Farklı molekül ağırlıklarında kitosan ile işlem görmüş ve nane ile boyanmış yün kumaşların boyanma ve haslık özelliklerinin değerlendirilmesi

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#### Abstract

Chitosan solutions were prepared by dissolving chitosan polymers, which were provided in three different molecular weight as low, medium and high, in acetic acid solution and were applied to wool fabrics. After chitosan treatment, the half of the samples were dyed with dried mint by mordanting with potassiumaluminumsulphate and another half of the samples were dyed with dried mint without mordanting. In addition, mordanted and unmordanted dyeing processes were also applied to the samples that were not treated by chitosan for comparison. Following the dyeing processes, the color values of the samples were measured via spectrophotometer by selecting the wool sample dyed with mint only as a reference. Then, the samples were exposed to washing, rubbing and light fastness tests and evaluated. Moreover, the color values of the samples after washing were measured again in order to determine the effect of washing process to color yield. From the results, it was observed that wool samples dyed with mint were in yellow and green colors and chitosan treatment had positive effects on color yield. Mordanting process caused for the wool samples to be in yellower color shades and to significant changes in color yield. Washing process decreased the color yield in all samples. Rubbing and light fastness values were found to be in acceptable limits for natural dyeing. On the other hand, chitosan treatment in different molecular weights was not found to be significant but generally medium molecular weight chitosan resulted in the most available one.

**Keywords:** Natural dyeing, Mint (Mentha), Mordanting, Potassiumaluminumsulphate, Chitosan, Wool.

#### Öz

Çalışmada düşük, orta ve yüksek olmak üzere üç farklı molekül ağırlığında kitosan polimerleri asetik asit çözeltisinde çözünerek hazırlanmış ve yün kumaşlara uygulanmıştır. Kitosan ile ön işlemin ardından kumaşların yarısı Potasyum alüminyum sülfat ile mordanlandıktan sonra diğer yarısı ise mordanlanmadan kuru nane ile boyanmıştır. Ayrıca karşılaştırma amacıyla kitosan ile işlem yapılmadan mordanlı ve mordanlısız boyama işlemleri de gerçekleştirilmiştir. Boyama işlemlerinin tamamlanmasından sonra spektrofotometre aracılığı ile yün kumaşların renk değerleri yalnızca nane ile boyanmış yünlü kumaş standart alınarak ölçülmüştür. Daha sonra kumaşlar, yıkama, sürtme ve ışık haslığı testlerine tabi tutulmuş ve değerlendirilmiştir. Ayrıca yıkama işleminin renk verimine etkisini belirlemek için numunelerin yıkama sonrası renk değerlerine de bakılmıştır. Sonuç olarak yünlü kumaşların nane ile sarı ve yeşil renk tonları verdiği, kitosan ile ön işlemin renk verimine olumlu etkisinin olduğu gözlenmiştir. Mordan uygulaması, yünlü kumaşların renginin sarı tonlarına yaklaşmasına ve renk veriminde belirgin bir değişime neden olmuştur. Yıkama işlemi tüm numunelerde renk verimini düşürmüştür. Sürtme ve ışık haslık değerleri, doğal boyamalar açısından kabul edilebilir seviyelerde bulunmuştur. Diğer taraftan, farklı molekül ağırlığında kitosan uygulamasının önemli bir etkisi olmaması ama genel anlamda orta molekül ağırlığının uygun olabileceği sonucuna ulaşılmıştır.

**Anahtar Kelimeler:** Doğal boyama, Nane, Mordanlama, Potasyumalüminyumsülfat, Kitosan, Yün.

## 1 Introduction

Natural dyeing is a technique used since 4000 B.C. till now in World history and has remained its importance especially in wool and felt dyeing in present time [1]-[5]. Natural dyeing processes have been performed by extraction of natural plants or living organisms like crustaceans and by application of this extract to natural fibers like cotton, wool and silk with the help of acidic metal salts [1],[2],[4],[5]. Except for plant and animals, mineral sources like clay, ochre, ferric oxide and ultramarine pigments can also be used for natural dyeing too [4],[5]. But natural dyeing from plant sources has commonly been made due to its advantages like to be cost-effective and simple and to have much color alternatives compared to other sources [1],[6]. Using of plants as color source depends on the compounds like quinone, alkaloid, carotenoid, tannin, phenolic acid and flavonoid in their chemical structures [3],[7],[8]. In the preceding studies, it has been reported that indigo is used for

blue, madder is used for red, indigo-madder mixture is used for purple, turmeric, buckthorn and reseda are used for yellow, indigo-reseda mixture is used for green and chamomile-madder mixture is used for orange color [2]-[4]. Natural dye plants are advantageous against synthetic dyes due to the fact that they do not have toxic, allergic and carcinogen effects and do not cause environmental pollution [2],[4]-[6],[8]-[14]. Moreover, some of these plants also have antimicrobial, antibacterial, antifungal, antioxidant and UV protection properties [2],[4],[10],[13],[15]-[18].

Mint that is a kind of plant belonged to the *Lamiaceae* (Labiatae) family is also general name for *Mentha* species [2],[16],[17]. There are three important mint species cultivated in the World as Pepper mint (*Mentha Piperita*), Japanese mint (*Mentha Arvensis*) and Spear mint (*Mentha spicata*). Apart from these, there are also some special mint species too. The production of mint is quite simple and can be made by seed, tiller and stem. After harvesting, the crop is dried in dark area

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or by special drying systems [17]. Mint, which is generally used for getting essential oil and spice, can also be used for textile dyeing to obtain khaki, dark green, yellow, pale yellow or brown colors depending on the content of mordant materials as reported in the previous studies [2],[4],[11],[16],[19].

Most of the natural dyes do not affinity to textile fibers and as a result of this fact, their bondings to the fibers are weak by hydrogen bonds and hydrophobic interactions [2],[4],[9]. Acidic metal salts, in other words, mordant materials are used to enable bonding and this bonding process of these materials to textile fibers is called as mordanting [2],[3],[9],[10],[12],[20]. Metal salts lead natural dyes to adsorb on the fiber surface and to become complex. So that, color yields and fastness properties of dyed textile surfaces are improved [3],[6],[9],[12],[13],[20]. In addition, different colors or different shades of the same color can also be obtained by using different mordant materials with one kind of extract [6],[9],[12],[20]. On the other hand, besides the much color alternatives, they have some disadvantages like having carcinogen or toxic properties, causing ecological problems and being inadequate and these disadvantages limit their applications [2],[21]. Among the metal salts, potassiumaluminumsulphate is known to be the most preferred mordant material due to be abundant, pure, ecologic and to enable bright color shades [2],[4],[21].

Chitosan is natural biopolymer and can be obtained by deacetylation of the chitin that exists in the crab and shrimp shells [15],[18],[22]-[26]. The molecular weight of chitin and chitosan can alter depending on the source and deacetylation degree and this fact directly affects the solubility, film forming ability and bonding properties of the chitin and chitosan [22]-[24]. For instance, chitosan can easily be solved in acidic pH values while chitin can not be solved in many organic solvents [15],[22]-[25]. To make the chitosan dissolved, generally formic acid, acetic acid and lactic acid have been used [23],[25]. Among these, the most preferred one is acetic acid as reported in the literature [15],[23]. Chitosan can be used in many textile processes, e.g. antimicrobial finishing, dyeing improvement and antifelting of wool via its distinctive properties as nontoxicity, biodegradability and reactivity with anionic materials due to the cationic chemical structure [4],[15],[18],[22]-[28].

The effect of chitosan treatment on wool dyeing was studied before by a few studies. For instance, Mohamed et al. 2015 evaluated the dyeability and antimicrobial activity of wool fibers pretreated with chitosan and dyed with synthetic (reactive) dyes and compared the chitosan application in different molecular weights for reactive dyeing [29]. Giri Dev et al. 2009 applied natural (henna) dye along with chitosan to impart antimicrobial characteristics and to increase dye uptake of wool fabrics [30]. Arik et al. 2012 studied the effect of chitosan on natural dyeability and antibacterial activity of wool fabrics and used natural dye plant, *Reseda Luteola* [31]. But in these two studies, the effects of the chitosan in different molecular weights were not compared in detail for natural dyeing. Moreover, natural dyeing with mint was not much studied as well. Kızıl and Kayabaşı, 2006; Tutak et al. 2014 and Eser et al. 2017 investigated the dyeing potential of dried and fresh forms of mint on wool fibers [11],[16],[19]. But they did not apply chitosan. So, dissimilarly from preceding studies, in this study, the effects of chitosan in different molecular weights on dyeing and fastness properties of wool fabric before natural dyeing with mint were firstly evaluated.

## 2 Material and method

### 2.1 Material

Mill scoured and washed 100% wool fabric weighing 166 g/m<sup>2</sup> (warp: 30 thread/cm, weft: 30 thread/cm) was used in this study. Dried mint (*Mentha spicata*) was supplied from local store as a natural colorant and potassiumaluminumsulphate was supplied from Merck as a mordanting material. Chitosan polymers in different molecular weights as low (Molecular weight: 70 000 Da and Deacetylation degree: 83.7%), medium (Molecular weight: 150 000 Da and Deacetylation degree: 85.5%) and high (Molecular weight: 375 000 Da and Deacetylation degree: 87.8%) were purchased from Sigma Aldrich and acetic acid (98%) used for dissolution of chitosan was supplied from Merck.

### 2.2 Method

#### 2.2.1 Chitosan pretreatment

Three different chitosan polymers as low, medium and high molecular weights were taken in two concentrations (0.5 and 2% w/v), added to acetic acid solution in the concentration of 2% v/v and stirred in room temperature till ensuring the homogeneity. The wool fabrics were dipped in the solutions, padded with the wet pick up of 80% in laboratory type horizontal padding machine (Prowhite Y002), dried at 90 °C for 3 min. and finally cured at 150 °C for 1 min. in laboratory type stenter (Prowhite Y003).

#### 2.2.2 Mordanting

Potassiumaluminumsulphate ( $KAl(SO_4)_2 \cdot 12H_2O$ ) was used as mordanting material and pre-mordanting method was applied to wool fabric. For this aim, mordant was taken as 20% (w/w) of wool weight and liquor ratio was adjusted as 1:30. Mordanting process was carried out at 100 °C for 60 min. in laboratory type dyeing machine (SandoLab SUPERMAT 6). Following, mordanted wool fabric samples were allowed to dry in room temperature.

#### 2.2.3 Mint dyeing

For dyeing process, dried mint leaves were prepared as 50% (w/w) of wool weight and liquor ratio was adjusted as 1:30. Dyeing process was carried out at 100 °C for 60 min. in laboratory type dyeing machine (SandoLab SUPERMAT 6). Then, dyed wool fabric samples were cleaned from the mint residues by washing and allowed to dry in room temperature.

#### 2.2.4 Color measurement

The colorimetric data of the samples were measured according to CIE Lab standart methods in spectrophotometer (Datacolor 600™).  $K/S$  values were calculated using the Kubelka-Munk equation as follows;

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

Where ( $K$ ) is the adsorption coefficient, ( $R$ ) is the reflectance and ( $S$ ) is the scattering coefficient. In addition, CIE  $L^*$ ,  $a^*$ ,  $b^*$ ,  $C^*$ ,  $h^\circ$ ,  $dE^*$  values were also determined where  $L^*$  is lightness,  $a^*$  is redness (+ve) or greenness (-ve),  $b^*$  is yellowness (+ve) or blueness (-ve),  $C^*$  is chroma,  $h^\circ$  is hue angle and  $dE^*$  is total color difference. For each sample, five measurements were made and mean values were calculated.

### 2.2.5 Washing fastness test

Washing fastness test was carried out according to ISO 105:C06 A2S standard method at 40°C for 30 min. with 4 g/L standard detergent (ECE) in SDL ATLAS M228 Rotawash machine. The change in colour and staining were evaluated using a grey scale between 1 and 5.

### 2.2.6 Rubbing fastness test

Rubbing fastness test was carried out according to ISO 105:X12 standard method as dry and wet in James Heal machine and evaluated using a grey scale between 1 and 5.

### 2.2.7 Light fastness test

Light fastness test was carried out according to ISO 105:B02 standard method and evaluated using a blue scale between 1 and 8.

## 3 Results and discussion

### 3.1 Colorimetric data results

In the study, dried mint leaves as natural colorant and potassiumaluminumsulphate as a mordanting material were used. Moreover, treatment with chitosan polymers in different molecular weights was also applied to wool fabrics before dyeing and the effects were evaluated.

The colors of mint dyed samples are given in Table 1.

According to the Table 1, mint dyed wool fabrics were found to be in khaki, dirty yellow and mustard yellow colors. It was clearly observed that mordanting process caused the colors to be in yellower shades and chitosan treatment caused high color yield. This fact confirmed the results of related studies [16],[29],[30],[31].

It has already known that mint type of *Mentha spicata* is rich in carvone that is a kind of terpenoid [16]. In this study, the colors of the mint dyed samples were attributed to this compound and the color change after mordanting was thought to be due to the change in light absorption and reflectance properties depending on the complex formation of carvone with metal ion of mordant.

Wool fabrics catch anionic dyestuffs via their amine (-NH<sub>2</sub>) groups and mordanting materials strength this bonding by bridging the auxochrome groups of dyestuffs to wool samples [3]. On the other hand, chitosan biopolymer is adsorbed to wool by hydrogen bonding, electrostatic forces and Van der Waals interactions and increases the dye adsorption on the wool surface due to its amine (-NH<sub>2</sub>) groups [18]. So, darker colors in higher chitosan concentration was attributed to this fact.

Since the mordanting process led to change in color shades, the colorimetric data were separately evaluated for mordanted and for unmordanted samples. Thereby, the colorimetric data for unmordanted samples before washing and after washing are given in Tables 2 and 3 respectively, while the colorimetric data for mordanted samples before washing and after washing are given in Tables 4 and 5 respectively.

Without mordanting, dark green and dirty yellow colors were obtained in the mint dyed wool samples and that  $h^\circ$  (hue angle) was between 85° and 92° verified this fact. When the  $K/S$  (color strength) values were considered, it was observed that chitosan treatment led to increase in color yield. Moreover, the increase in chitosan concentration provided darker colors, so that it was concluded that it should be studied with high chitosan concentration for dark colors. When the molecular


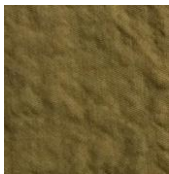



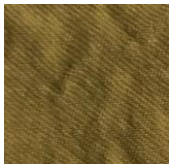


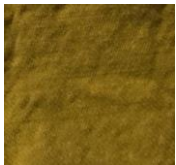
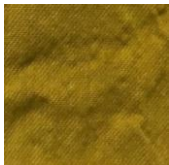



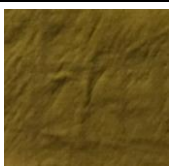
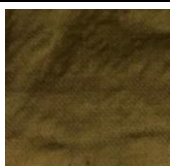






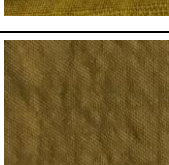

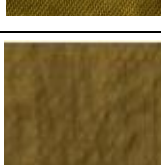




weights of the chitosan polymers were compared, it was found that although there were no significant differences, medium molecular weight chitosan could be more available. The highest color yield was provided by the medium molecular weight chitosan in 2% concentration.  $L^*$  (lightness) values decreased depending on the increase in color darkness.  $a^*$  values passed from negative values to positive values that mean greenness decreased and redness increased.  $b^*$  values kept on the positive values in the positive direction, so yellowness increased while blueness decreased.  $C^*$  (chroma) and  $dE^*$  (total color difference) values were found to increase in parallel with color yield too.

Dyed samples were subjected to washing process and their colorimetric data were measured again. Accordingly, decreases in color yield were observed after washing. This fact was attributed to the ionation of hydroxyl groups of dye molecules and decomposition of some part of the dyestuff because of the alkaline medium of standard detergent solution as reported in another study [16].  $L^*$  values increased accordingly to the decrease in color yield. Since  $a^*$  values increased with respect to before washing, it was determined that greenness decreased.  $b^*$  values also increased with respect to before washing, so the yellowness tendency in color shade was proved.  $h^\circ$  values verified this tendency too.  $C^*$  and  $dE^*$  values changed in accordance with color yield. In mordanted and mint dyed samples, the colors were found to be bright dark green and mustard yellow and that  $h^\circ$  (hue angle) was between 83° and 87° verified this fact. Color strength ( $K/S$ ) values were found to be quite high when compared to unmordanted samples and chitosan treatment promoted this increase. The change in molecular weight of chitosan polymer resulted to be insignificant since usage of different molecular weight chitosan polymers did not show distinct difference. The fact that  $L^*$  values were higher than unmordanted samples showed that the mordanting process led to bright and vivid colors. Since  $a^*$  values increased, it was determined that greenness decreased and redness increased.  $b^*$  values clearly increased in comparison with unmordanted samples and confirmed the evident change in yellowness.  $C^*$  and  $dE^*$  values were found to increase in parallel with color yield too. After washing process, decrease in color yield in mordanted samples was observed similarly to the unmordanted samples. Decrease in color yield caused  $L^*$  values to increase.  $a^*$  and  $b^*$  values increased when compared to the samples before washing and showed that greenness decreased and yellowness increased.  $C^*$  and  $dE^*$  values changed in accordance with color yield.

### 3.2 Washing fastness test results

Washing fastness test results of the unmordanted dyed samples are given in Table 6 while washing fastness test results of the mordanted dyed samples are given in Table 7. Color change of the unmordanted dyed samples were evaluated as medium level. Chitosan treatment did not cause any important change. On the other hand, the washing fastness values for staining were evaluated as quite good. Color change of the mordanted dyed samples were evaluated as medium and low. Especially, the color of the sample without chitosan treatment was quite different. But in the chitosan treated samples color change showed one point improvement and this fact showed positive effect of chitosan treatment in mordanted dyeing to washing. On the other hand, the washing fastness values for staining were evaluated as quite good likewise the unmordanted dyed samples.

Table 1. The colors of the mint dyed samples.

Sample	Before Washing	After Washing	Sample	Before Washing	After Washing
Mint dyed only			Mordanted and mint dyed		
0.5% LMWC treated and mint dyed			2% LMWC treated and mint dyed		
0.5% LMWC treated, mordanted and mint dyed			2% LMWC treated, mordanted and mint dyed		
0.5% MMWC treated and mint dyed			2% MMWC treated and mint dyed		
0.5% MMWC treated, mordanted and mint dyed			2% MMWC treated, mordanted and mint dyed		
0.5% HMWC treated and mint dyed			2% HMWC treated and mint dyed		
0.5% HMWC treated, mordanted and mint dyed			2% HMWC treated, mordanted and mint dyed		

LMWC: Low molecular weight chitosan, MMWC: Medium molecular weight chitosan, HMWC: High molecular weight chitosan.

Table 2. Colorimetric data of the unmordanted mint dyed samples before washing.

Sample	$K/S$	$L^*$	$a^*$	$b^*$	$C^*$	$h^\circ$	$dE^*$
Mint dyed only	6.76	57.41	-0.91	20.97	22.88	92.33	Reference
0.5% LMWC treated and mint dyed	7.30	53.52	2.48	24.75	25.18	85.76	5.26
0.5% MMWC treated and mint dyed	8.03	51.99	2.31	24.12	25.88	86.65	7.83
0.5% HMWC treated and mint dyed	7.41	53.13	2.38	24.21	25.70	86.55	6.18
2% LMWC treated and mint dyed	8.83	49.32	1.59	23.67	25.16	88.15	8.58
2% MMWC treated and mint dyed	9.26	47.98	1.53	23.19	26.79	89.31	9.38
2% HMWC treated and mint dyed	8.92	49.12	1.58	23.58	26.29	88.30	9.15

LMWC: Low molecular weight chitosan, MMWC: Medium molecular weight chitosan, HMWC: High molecular weight chitosan.

Table 3. Colorimetric data of the unmordanted mint dyed samples after washing.

Sample	K/S	L*	a*	b*	C*	h°	dE*
Mint dyed only	6.31	58.41	1.87	22.80	20.99	85.30	Reference
0.5% LMWC treated and mint dyed	6.51	56.33	2.95	26.69	24.36	84.04	2.95
0.5% MMWC treated and mint dyed	6.72	55.19	2.46	25.05	24.79	84.46	3.49
0.5% HMWC treated and mint dyed	6.53	55.39	2.84	25.84	24.75	84.18	3.38
2% LMWC treated and mint dyed	7.22	53.23	2.16	26.11	25.16	84.80	3.91
2% MMWC treated and mint dyed	7.96	51.09	2.05	24.93	26.49	85.15	4.72
2% HMWC treated and mint dyed	7.72	52.40	2.07	25.80	26.26	84.91	4.46

LMWC: Low molecular weight chitosan, MMWC: Medium molecular weight chitosan, HMWC: High molecular weight chitosan.

Table 4. Colorimetric data of the mordanted mint dyed samples before washing.

Sample	K/S	L*	a*	b*	C*	h°	dE*
Mint dyed only	6.76	57.41	-0.91	20.97	22.88	92.33	Reference
Mordanted and mint dyed	20.30	56.39	2.79	35.94	38.29	83.72	19.13
0.5% LMWC treated, mordanted and mint dyed	21.61	55.07	3.45	35.24	39.17	84.89	21.97
0.5% MMWC treated, mordanted and mint dyed	23.50	54.47	2.96	33.69	42.98	86.75	23.66
0.5% HMWC treated, mordanted and mint dyed	23.11	54.82	3.20	34.08	42.15	85.59	22.12
2% LMWC treated, mordanted and mint dyed	23.02	54.89	2.58	33.73	41.96	85.15	22.06
2% MMWC treated, mordanted and mint dyed	23.67	54.16	2.39	33.10	43.16	87.41	24.79
2% HMWC treated, mordanted and mint dyed	23.62	54.49	2.46	33.38	43.10	85.92	22.64

LMWC: Low molecular weight chitosan, MMWC: Medium molecular weight chitosan, HMWC: High molecular weight chitosan.

Table 5. Colorimetric data of the mordanted mint dyed samples after washing.

Sample	K/S	L*	a*	b*	C*	h°	dE*
Mint Dyed only	6.31	58.41	1.87	22.80	20.99	85.30	Reference
Mordanted and mint dyed	13.32	57.73	3.92	43.00	33.26	84.15	11.47
0.5% LMWC treated, mordanted and mint dyed	14.26	57.56	3.91	44.16	33.45	84.74	11.82
0.5% MMWC treated, mordanted and mint dyed	15.70	55.80	3.56	43.14	34.10	84.95	12.02
0.5% HMWC treated, mordanted and mint dyed	15.19	56.68	3.74	42.93	33.86	84.76	11.87
2% LMWC treated, mordanted and mint dyed	15.30	56.09	2.98	41.79	33.87	84.88	11.90
2% MMWC treated, mordanted and mint dyed	16.55	54.88	2.63	40.34	36.05	85.18	12.61
2% HMWC treated, mordanted and mint dyed	15.92	55.19	2.75	41.43	35.37	84.97	12.13

LMWC: Low molecular weight chitosan, MMWC: Medium molecular weight chitosan, HMWC: High molecular weight chitosan.

Table 6. Washing fastness test results of the unmordanted dyed samples.

Sample	Color Change	Staining					
		Wool	Polyacrylnitril	Polyester	Polyamide	Cotton	Acetate
Mint dyed only	3	4-5	5	5	5	4-5	5
0.5% LMWC treated and mint dyed	3-4	4-5	5	5	5	4-5	5
0.5% MMWC treated and mint dyed	3-4	4-5	5	5	5	4-5	5
0.5% HMWC treated and mint dyed	3-4	4-5	5	5	5	4-5	5
2% LMWC treated and mint dyed	3	5	5	5	5	5	5
2% MMWC treated and mint dyed	3	5	5	5	5	4-5	5
2% HMWC treated and mint dyed	3	5	5	5	5	5	5

LMWC: Low molecular weight chitosan, MMWC: Medium molecular weight chitosan, HMWC: High molecular weight chitosan.

Table 7. Washing fastness test results of the mordanted dyed samples.

Sample	Color Change	Staining					
		Wool	Polyacrylnitril	Polyester	Polyamide	Cotton	Acetate
Mordanted and mint dyed	2	4-5	5	5	5	4-5	5
0.5% LMWC treated, mordanted and mint dyed	3	5	5	5	5	5	5
0.5% MMWC treated, mordanted and mint dyed	3	5	5	5	5	5	5
0.5% HMWC treated, mordanted and mint dyed	3	5	5	5	5	5	5
2% LMWC treated, mordanted and mint dyed	3	5	5	5	5	5	5
2% MMWC treated, mordanted and mint dyed	3	5	5	5	5	5	5
2% HMWC treated, mordanted and mint dyed	3	5	5	5	5	5	5

LMWC: Low molecular weight chitosan, MMWC: Medium molecular weight chitosan, HMWC: High molecular weight chitosan.

### 3.3 Rubbing and light fastness test results

Rubbing and light fastness results of the unmordanted dyed samples are given in Table 8, while rubbing and light fastness results of the mordanted dyed samples are given in Table 9.

Dry rubbing fastness values were evaluated as good in unmordanted dyed samples. Since wet rubbing fastness values were lower than dry rubbing fastness values, wet rubbing fastness values were evaluated as medium and good.

Chitosan treatment led to decrease in rubbing fastness of unmordanted samples and this was attributed to the fact that chitosan treated samples had darker colors than mint dyed only. Light fastness values of unmordanted samples were found to be moderate for natural dyeing and chitosan treatment did not cause any significant change. Only, the light fastness values of the 2% medium molecular weight and 2% high molecular weight chitosan treated samples were found to be low in comparison with the others due to the high color yield ( $K/S$ ) and chroma ( $C^*$ ) values as reported in other studies about natural dyeing [9],[16],[32].

Rubbing fastness values of mordanted dyed samples were evaluated as medium in general. The highest rubbing fastness values were obtained in the sample without chitosan treatment. In the other samples, the rubbing fastness values decreased to medium levels, so it was concluded that chitosan treatment affected negatively the rubbing fastness. Light fastness values were found to be quite close to the values of unmordanted dyed samples, so it was understood that mordanting process had no prominent impact on light fastness. Similarly, chitosan treatment did not cause any significant change in the light fastness too.

### 4 Conclusion

The wool fabrics treated by chitosan polymers in different molecular weights were dyed with dried mint by mordanting and unmordanting. While in the samples dyed without mordanting the colors were dark green and dirty yellow, brighter and yellower shades were obtained in the samples dyed by mordanting. Chitosan treatment affected positively the

color yield and washing fastness of the mordanted dyed samples. High chitosan concentration led to high color yield. Washing process caused decreases in color yields due to the deteriorative effect of detergent. Rubbing and light fastness values were found to be in medium and good levels. When the molecular weight difference of chitosan polymers was considered, it was observed that medium molecular weight chitosan could be available despite the little differences. Consequently, it was concluded that mordanting process was important in terms of color yield and chitosan treatment had positive contributions regardless of molecular weight. Moreover, this study was significant in terms of sustainable environment owing to the fact that natural, ecological and human health sensitive materials were used.

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Table 8. Rubbing and light fastness results of the unmordanted dyed samples.

Sample	Rubbing		Light
	Dry	Wet	
Mint dyed only	5	4-5	5
0.5% LMWC treated and mint dyed	4-5	4	5
0.5% MMWC treated and mint dyed	4-5	4	4-5
0.5% HMWC treated and mint dyed	4-5	3	4-5
2% LMWC treated and mint dyed	4	3-4	4-5
2% MMWC treated and mint dyed	4	3	4
2% HMWC treated and mint dyed	4	3	4

LMWC: Low molecular weight chitosan, MMWC: Medium molecular weight chitosan, HMWC: High molecular weight chitosan.

Table 9. Rubbing and light fastness results of the mordanted dyed samples.

Sample	Rubbing		Light
	Dry	Wet	
Mordanted and mint dyed	4-5	4	4-5
0.5% LMWC treated, mordanted and mint dyed	4	3-4	4-5
0.5% MMWC treated, mordanted and mint dyed	4	3-4	4-5
0.5% HMWC treated, mordanted and mint dyed	4	3-4	4-5
2% LMWC treated, mordanted and mint dyed	4	3	4-5
2% MMWC treated, mordanted and mint dyed	3-4	3	4
2% HMWC treated, mordanted and mint dyed	3-4	3	4

LMWC: Low molecular weight chitosan, MMWC: Medium molecular weight chitosan, HMWC: High molecular weight chitosan.

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