EFFECT OF CHITOSAN ON NATURAL DYEABILITY AND ANTIBACTERIAL ACTIVITY OF WOOL FABRICS*

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ABSTRACT

In this study, the effect of the pretreatment with chitosan biopolymer on the functional and aesthetic properties of wool fabrics which will be dyed with natural dye was investigated. As a natural dye plant, Reseda Luteola commonly grown in Mediterranean countries was used. Optimum dyeing conditions were determined by studying various parameters such as mordant type and concentration, dye concentration, dyeing temperature and time. Then, wool fabrics pretreated with chitosan solutions in different concentrations were dyed according to these optimum conditions. The treated samples were evaluated in terms of colour yield, antibacterial activity and fastness properties. It was observed that chitosan distinctively increased both antibacterial activity and colour yield of wool fabrics.
Keywords: Chitosan, Natural Dye, Reseda Luteola, Antibacterial, Wool.

KİTOSANIN YÜNLÜ KUMAŞLARIN DOĞAL BOYALARLA BOYANABİLİRLİK VE ANTİBAKTERİYELLİK ÖZELLİKLERİNE ETKİSİ

ÖZET

Bu çalışmada, kitosan biyopolimeri ile ön işlemin, doğal boyama yapılacak yünlü kumaşların fonksiyonel ve estetik özellikleri üzerindeki etkisi araştırılmıştır. Doğal boyama bitkisi olarak, Akdeniz ülkelerinde yaygın olarak yetişen Reseda Luteola (Muhabbet Çiçeği) kullanılmıştır. İdeal boyama koşulları, mordan çeşidi ve konsantrasyonu, boyarmadde konsantrasyonu, boyama sıcaklığı ve süresi gibi çeşitli parametreler değiştirilerek belirlenmiştir. Ardından, farklı konsantrasyonlarda kitosan çözeltileri ile ön işlem görmüş yünlü kumaşlar belirlenen ideal boyama koşullarına göre boyanmıştır. İşlem gören numuneler, renk verimi, antibakteriyel aktivite ve haslık özellikleri açısından değerlendirilmiştir. Kitosanın yünlü kumaşların hem antibakteriyel aktivitelerini hem de renk verimlerini belirgin bir şekilde arttırdığı gözlenmiştir.
Anahtar Sözcükler: Kitosan, Doğal Boya, Reseda Luteola, Antibakteriyel, Yün.

Introduction: Increased environmental consciousness and consumer demands have taken attention to natural textile surfaces with functional properties and to polymers that can be used to give these properties (Samanta and Agarwal, 2009:384-399, Osman et al., 2010:28-39). Chitosan (Fig. 1) which has a similar structure to cellulose and is a natural polymer has been widely used in textile industry for improving the properties like color yield, antibacterial and antifelting of the textile surfaces (Giri Dev et al., 2009:646-650, Kampeerapappun et al., 2010:95-104, Suitcharit et al., 2010:27-31). The cationic form of chitosan in acidic solution plays a role in not only governing its solubility but also acting as an active site. In the field of textile the higher the active site of chitosan favors the higher the dye adsorption (including natural dye) as well as film formation on the fiber surface (Kittinaovarat, 2004:155-164, Suitcharit et al., 2010: 27-31). A number of researchers reported the use of chitosan in dyed textile surfaces for enhanced characteristics (Shin et al., 2009: 204-207) investigated the efficacy of chitosan treatment to improve dye uptake of bamboo colorants on cotton and ramie in terms of dye uptake, color, and fastness. Ramie showed higher improvement of dye uptake than cotton. The dyed fabrics gave 99% of bacteria reduction rate against both of Staphylococcus aureus and Klebsiella pneumonia (Giri Dev et al., 2009: 646-650) applied Henna dye along with chitosan to impart antimicrobial characteristics to wool fabrics and proved that the chitosan treated wool fabrics showed increased antimicrobial activity and dye uptake. Since the fastness properties of natural dyed fabrics are weak, they have been pretreated with various metal salts as mordant material to improve the fixation of dyestuff to fabric and to obtain different color shades (Guesmi et al., 2012: 493-499) studied dyeing properties and colour fastness of wool pretreated by different mordant types and dyed with indicaxanthin natural dye. They found that the colour yield of the samples increased in the order of the dyeing using $KAl(SO_4)_2 > MnSO_4 > CoSO_4 > FeSO_4 >$ none $> ZnSO_4 > CuSO_4$ and $KAl(SO_4)_2$ and $CoSO_4$ mordants had good light fastness. Nowadays, the use of natural mordant dyes (biomordants) has taken attention too (Kamel et al., 2011:289-307) investigated the dyeing properties of wool with a mixture of natural dyes. The results indicated that dyeing with combination of mordants improved the washing and light fastness from moderate to very good fastness properties and a large range of shades was obtained. Although it has been proved that chitosan improved some properties of the textile surfaces, the combined effect of chitosan and natural dyes on dyeability and antibacterial activity of wool fabrics has not been fully investigated. Hence the aim of the present study is to evaluate the effect of chitosan on natural dyeability and antibacterial activity of wool fabrics.

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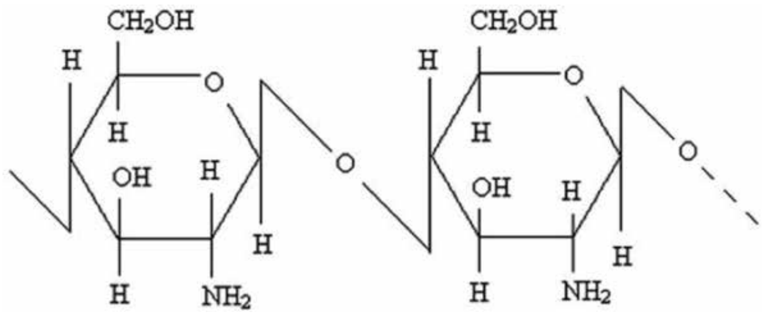

Figure 1: Chemical structure of chitosan (Giri Dev et al., 2009)

Experimental (Material): In the study, woven wool fabric with a weight of 194 g/m2 was used. It was pretreated and ready for dyeing. As a natural dye plant, Reseda Luteola commonly grown in Mediterranean countries was used. As a mordant, two different mordant types were selected. First mordant was potassium aluminum sulphate (KAl(SO4)2) from metallic origin and the second one was sumac (Rhus coriaria) from natural origin (biomordant). Sumac grows in subtropical and temperate regions throughout the world and is widely used as a kind of spice. In this study, the dried sumac was used and directly added to the mordant bath.
Method (Dyeing Process): Firstly, optimum dyeing conditions were determined by studying various parameters such as mordant concentration, dye concentration, dyeing temperature and time. The study was performed in two groups since two different types of mordants were used. In the first step, optimum mordant concentration was studied. Wool fabrics were pretreated with potassium aluminum sulphate and sumac solutions with the concentrations of 1%, 5%, 10%, 20% and 30% and then dyed in the same bath conditions. In the second step, optimum dye concentration was studied. Wool fabrics pretreated by optimum mordant concentration were dyed with the dye concentrations of 1%, 5%, 10%, 20% and 30%. In the third step, wool fabrics were dyed in different temperatures (60, 80 and 100°C) and in different times (30, 45, 60, 75 and 90 min.). The hardness value of the water used in the solutions was 10°F.
Chitosan Application: Chitosan solutions were freshly prepared by dissolving the biopolymer in pure water containing 2% acetic acid. Three different chitosan concentrations (0.5%, 0.75% and 1%) were studied. Samples were immersed to the solutions for 5 min., padded with a wet pick up of 90±1%, dried at 90°C for 3 min. and cured at 150°C for 1 min. After chitosan application, the samples were dyed with the optimum dyeing conditions.
Evaluation Methods: The dyed samples were evaluated in terms of CIE L*, a*, b* values, color efficiencies (K/S) in Hunterlab Color Quest II spectrophotometer (D65/10°) and assessed in terms of washing (ISO 105-C02), rubbing (ISO 105-X12), perspiration (ISO 105-E04) and light (ISO 105-B02) fastnesses. The antibacterial properties of the samples were tested according to ASTM E2149-01 against the gram positive bacteria Staphylococcus aureus and gram negative bacteria Klebsiella pneumonia.
Results and Discussion (The Effect of Mordant Concentration on Colour Yield of Dyed Samples): The effect of mordant concentration on colour yield (K/S values) of dyed samples is shown in Table 1.

Table 1: K/S values of dyed wool samples pretreated with two types of mordant at different mordant concentration

Mordant Type	Mordant Concentration (%)	Colour Yield (K/S)
Un-mordanted-dyed Wool	-	1,0329
Potassium aluminum sulphate	1	3,7931
	5	3,7541
	10	3,7596
	20	2,9831
	30	2,7776
Sumac	1	1,1603
	5	1,3963
	10	1,3521
	20	1,2857
	30	1,1184

Dyestuff 10%, Temp. 100°C, Time 60. min.

From the Table 1, it was observed that the optimum mordant concentration for potassium aluminum sulphate was 1%, whereas 5% for sumac.
The Effect of Dye Concentration on Colour Yield of Dyed Samples: The effect of dye concentration on colour yield (K/S values) of dyed samples is shown in Table 2.

Table 2: K/S values of wool samples pretreated at optimal mordant concentration and dyed with Reseda Luteola at different dye concentration

Mordant Type	Dye Concentration (%)	Colour Yield (K/S)
Potassium aluminum sulphate (1%)	1	0,8159
	5	2,4173
	10	3,7931
	20	5,5807
	30	4,3211
Sumac (5%)	1	0,7292
	5	0,9083
	10	1,4963
	20	1,9217
	30	1,7734

Temp. 100°C, Time 60. min.

From the Table 2, it was observed that the optimum dyestuff concentration was 20% for both potassium aluminum sulphate and sumac. The optimum concentrations mean the saturation levels of the fibres as well.

The Effect of Dyeing Temperature and Time on Colour Yield of Dyed Samples: The effects of dyeing temperature and process time on colour yield (K/S) of dyed wool samples are given in Tables 3 and 4 respectively.

Table 3: K/S values of wool samples dyed at different temperatures

Mordant Type	Dyeing Temperature (°C)	Colour Yield (K/S)
Potassium aluminum sulphate (1%)	60	3,9504
	80	5,0417
	100	5,5807
Sumac (5%)	60	1,5726
	80	1,5546
	100	1,9217

Dyestuff conc. 20%, Temp. Time 60. min.

As seen in the Table 3, color yield of dyed wool increased at high temperatures. In Table 4, it was observed that dye in the fibre and the dyebath reached to equilibrium after 60 minutes.

Table 4: K/S values of wool samples dyed at 100°C but for different process times

Mordant Type	Dyeing Process Time (min.)	Colour Yield (K/S)
Potassium aluminum sulphate (1%)	30	4,9739
	45	5,5000
	60	5,5807
	75	5,3646
	90	5,2753
Sumac (5%)	30	1,0752
	45	1,8531
	60	1,9217
	75	1,3473
	90	1,3275

Dyestuff conc. 20%, Temp. 100°C

From the Tables 1-4, it was determined that the optimal dyeing conditions were 1% mordant, 20% dyestuff, 100°C temperature and 60 minute duration for the samples mordanted by potassium aluminum sulphate and 5% mordant, 20% dyestuff, 100°C temperature and 60 minute duration for the samples mordanted by sumac. After the optimal dyeing conditions were determined, the wool samples pretreated at different chitosan concentrations (0.5%, 0.75% and 1%) were dyed at these conditions and the colour yield, fastness properties and antibacterial activity of these samples were tested and compared.

Color Values of Dyed Samples: The effect of chitosan treatment on color yield and shade of the samples is shown in Table 5. From the Table 5, it was observed that chitosan application increased the color yield and the best results were obtained with the 1% chitosan concentration. This enhancement in (K/S) values of chitosan treated wool samples was attributed to the introduction of chitosan primary amino groups into the fibre structure.

Table 5: Color values of dyed samples

Mordant Type	Chitosan Conc. (%)	K/S	L*	a*	b*
Un-mordanted-dyed Wool	0	2,0584	73,80	0,21	24,11
	0.5	2,4615	72,84	0,36	24,26
	0.75	2,4991	72,72	0,49	24,84
	1	2,5873	72,60	0,57	25,08
Potassium aluminum sulphate (1%)	0	5,3807	70,38	-0,99	49,75
	0.5	5,6616	70,35	-0,26	49,78
	0.75	5,9178	70,26	-0,18	49,79
	1	5,9657	70,19	-0,13	49,87
Sumac (5%)	0	2,2217	72,69	1,67	24,81
	0.5	2,5998	72,51	1,64	24,14
	0.75	2,6172	72,42	1,53	24,07
	1	2,7407	72,23	1,55	24,03

Dyestuff 20%, Temp. 100°C, Time 60. min.

Mordanting process by the potassium aluminum sulphate was common but to minimize the hazardous effect of the agent to environment, sumac was also used as a biomordanting agent in this study. Since the mordanting process affected the color shade, color values (L, a, b) were also detected in addition to K/S values and compared with the un-mordanted-dyed samples. Lower L* values indicate that the sample becomes darker than control sample and it has been observed that L* values decreased with the increase in chitosan concentration and with the change in mordant type. Particularly, the fabrics mordanted with ($KAl(SO_4)_2$) exhibited the highest difference in color depth and shade. In Figure 2, the images of un-treated, un-mordanted-dyed and mordanted-dyed samples are presented. As seen, the sample mordanted with ($KAl(SO_4)_2$) is completely different.

(a) (b) (c) (d)

Figure 2: The images of the wool samples (a) un-treated (b) un-mordanted-dyed (c) mordanted with sumac-dyed (d) mordanted with ($KAl(SO_4)_2$)-dyed

Antibacterial Activity of Dyed Samples: The effect of chitosan treatment on antibacterial activity of the samples is given in Table 6. Antibacterial test results clearly indicated that chitosan application and mordanting process had a positive effect on antibacterial activity of the samples. It was observed that antibacterial activity improved with the increasing chitosan concentration. The most accepted mechanism for microbial inhibition by chitosan is the interaction of the positively charged chitosan with the negatively charged bacterial surface. This causes the leakage of intracellular substances and death of the cell (Giri Dev et al., 2009:646-650). The best results was obtained in the sample that were pretreated by 1% chitosan and 1% ($KAl(SO_4)_2$) mordanting agent and dyed.

Table 6: Antibacterial activity of dyed samples (% bacterial reduction)

Mordant Type	Chitosan Conc. (%)	Bacteria	
		Staphylococcus aureus	*Klebsiella pneumoniae*
Un-treated wool (control)	0	-	-
Un-mordanted-dyed wool	0	-	-
	0.5	73.03	30.77
	0.75	80.48	36.95
	1	93.70	67.44
Potassium aluminum sulphate (1%)	0	59.32	38.75
	0.5	88.13	44.78
	0.75	95.46	52.38
	1	99.99	86.40
Sumac (5%)	0	50.99	32.54
	0.5	76.18	42.50
	0.75	80.63	62.86
	1	95.22	79.51

No reduction was observed.

As seen from the Table 7, the fastness properties were found to be good and nearly same with un-mordanted-dyed sample. It was also observed that chitosan application decreased the fastness values to some extent (half point) in some cases. On the other hand, it was clearly seen that after washing and alkaline perspiration fastness tests, the color shades changed positively and more vivid and deeper color values were obtained after tests. This fact was attributed to the pH of the test solutions was highly alkaline and wool had amphoteric character.

Fastness Properties of Dyed Samples: The effect of chitosan treatment on fastness properties of the samples is shown in Table 7.

Table 7: Fastness properties of dyed samples

Mordant Type	Chi. Conc. (% w/v)	Washing fastness			Rubbing fastness		Perspiration fastness (Acidic)			Perspiration fastness (Alkaline)			Light Fastness
		A	C	W	Dry	Wet	A	C	W	A	C	W	
Un-mordanted-dyed Wool	0	4	4/5	4/5	5	5	4/5	5	5	4	4	4/5	6
	0.5	3/4	4	4/5	5	4/5	4/5	5	5	4	4/5	5	5/6
	0.75	3	4	4/5	5	4/5	4/5	5	5	4	4/5	5	5/6
	1	3	4	4/5	4/5	4	4/5	5	5	4	4/5	5	5/6
Potassium aluminum sulphate (1%)	0	4	5	5	5	5	4	5	5	3/4	4/5	5	6
	0.5	4	4/5	4/5	5	4/5	4/5	5	5	4	4/5	5	5/6
	0.75	4	4/5	4/5	5	4/5	4/5	5	5	4	4/5	5	5/6
	1	4	4	4/5	5	4/5	4/5	5	5	4	4/5	5	5/6
Sumac (5%)	0	3/4	4/5	5	5	5	4/5	5	5	4	4/5	5	6
	0.5	3/4	4	4/5	5	5	4/5	5	5	4	4/5	5	5/6
	0.75	3/4	4	4/5	5	4/5	4/5	5	5	4	4/5	5	5/6
	1	3/4	4	4/5	5	4/5	4/5	5	5	4	4/5	5	5/6

A: Alteration (change) in color C: Staining on cotton W: Staining on wool

Conclusion: Chitosan which is a non-toxic biopolymer was used to confer antibacterial activity and to increase the dye-uptake of the wool fabrics in this study. Mordanting processes and mordanting agents from different sources were also discussed. It was determined that chitosan application had positive effects on the samples and as a mordanting agent, (KAl(SO4)2) was found to give higher color yield than sumac. The fastness properties were observed to be good against washing, rubbing, light and perspiration and interestingly, the samples showed deep and vivid colors after washing.

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