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Grafting of alginate biopolymer/nano Ag as a clean antimicrobial and antioxidant agent
on the wool: Characterization and natural dyeing studies

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Abstract

There is a continuous search for sustainable materials and processes for dyeing and finishing of textiles to diminish the hazardous impact on the nature. In current study, the grafting of bio-composite Sodium Alginate- Silver nanoparticles (SA-Ag NPs) on the wool yarns was performed, and all samples were dyed with Cochineal and Madder dyes. The weight gain of the samples was measured to find the optimized SA-Ag NPs initial concentration, and the surface morphology of samples was studied by SEM-EDX. The color strengths of the treated samples were calculated, and the impacts of various parameters, including the initial dye concentration, pH, temperature, and duration were investigated. It was found that the pretreatment enhanced the dye-ability, antimicrobial, and antioxidant characteristics of the samples noticeably. To obtain the same color strength on the treated wool samples, one can use less amount of initial dye concentration, at a lower temperature, and for a shorter duration compared to the values needed for dyeing of untreated samples. The colorfastness characteristics of the treated samples remained the same, and no negative impact was observed.

The results clearly showed that the application of SA-Ag NPs on the wool samples could be considered as a green finishing process with promising antioxidant and antimicrobial activities. A very high level of antimicrobial and antioxidant efficiency (over 99%) was achieved after the pretreatment, which remained as high as 90% even after ten repeated washing cycles.

Keywords: Wool yarn, Sodium alginate/Ag, Natural dyes, Enhanced dyeability, antimicrobial, antioxidant

1-Introduction

The high surface area and moisture absorption of cotton and wool as the natural fibers, supplied a proper environment for the development of various microorganisms (Maryan et al., 2015; Ferrero et al., 2014; Rajendran and Anand, 2002; Gouda, 2011). Bacteria can spread infections, change the color, and reduce the strength of textiles. Hence, antimicrobial textile finishing is a very important treatment for hospital clothing, underwear, baby clothing, carpets, and sportswear. Antimicrobial textile finishing can be achieved by surface modification via chemical treatment using antimicrobial agents such as inorganic salts, or cationic polymers and surfactants. This treatment should ideally not reduce the mechanical properties, wear-ability, and comfort of the treated textile (Hou and Sun, 2013; Afzal et al., 2014; Nikolic et al., 2010; Zhuo and Sun, 2013).

Normally, a considerable amount of energy, water, and chemicals is required for dyeing and finishing of textiles, which may lead to increase the cost and harmful environmental effect of the final products (Zhuo and Sun, 2013; Dastjerdi et al., 2009; Harifi and Montazer, 2012; Zhuo and Sun, 2014). Therefore, there is a growing demand for green and sustainable textile finishing to decline the harmful environment result and cost (Ibrahim et al., 2010; El-Shafei et al., 2015;

Shahid et al., 2013). Lately, sustainable biomaterials such as alginate (Zahran et al., 2014; 49
Mihailovi'c et al., 2010), cyclodextrin (Dehabadi et al., 2014; Martin et al., 2013), chitosan 50
(Gaffer et al., 2012; Gouda and Keshk, 2010; Ferrero et al., 2014; Periolatto et al., 2013; He et 51
al., 2011), propolis (Sharaf et al., 2013), and collagen (Wang et al., 2004; Xu et al., 2013) have 52
been used for the extension of functional goods. The unique characteristics of alginate, such as 53
high gelling, and biocompatibility properties, has made it an interesting choice not only in 54
textile finishing but also in biomedical applications (Lin and Ciou, 2010; Chan et al., 2007; 55
Goh et al., 2012; Deze et al., 2012; Goh et al., 2008; Rani et al., 2011). The antimicrobial 56
activity of coated cotton fabrics with silver nitrate using alkali hydrolyzed alginate solution 57
was studied and excellent results was obtained (Bajpai et al., 2012; Zahran et al., 2014). Also, 58
treatment of cotton fabric with copper NPs in the presence of calcium alginate, and samples 59
had fair mechanical strength and strong antimicrobial activity (Mihailovi'c et al., 2010). In 60
another study, the modified polyester fabric with alginate and TiO₂ NPs showed an acceptable 61
UV protection efficiency and antibacterial activity even after several washing cycles. 62

Alginate is achieved from brown algae, and its physical-chemical characteristics generally 63
depend on the molecular weight of the uronate residues as well as the arrangement of the 64
copolymer (Paques et al., 2014; Sun and Tan, 2013). Alginate biopolymer with plenty of free 65
functional groups, including carboxyl and hydroxyl groups, is an appropriate compound for the 66
modification of textiles (Li et al., 2017). 67

Madder, with the scientific name *Rubia tinctorum* L. is an old and valuable natural dye, 68
including various anthraquinones such as Lucidine premeverside, Ruberythric acid, 69
Pseudopurpurin, Munjistine, Lucidine glucoside, Alizarin glucoside, Alizarine, 70
Xanthopurpurin, and Purpurin. The chemical structures of the first four species that are often 71
extracted in a mixture of water: ethanol (1:1) have been provided in Figure 1(a) (Derksen et 72
al., 2003). The mixture of compounds extracted from Madder has been used for textile 73

coloration since 2000 B.C. (Derksen et al., 2003; Manian et al., 2016). Madder was used as one of the most significant natural dyes for dyeing of wool yarns used in hand-woven carpets. Various shades can be obtained by using Madder with or without any mordants. The shades may change from light pink, orange, or purple without any mordants to a high color depth such as gray, brown, and black with different metallic mordants (Manian et al., 2016). The literature shows that the applications of Madder for dyeing and antimicrobial finishing of textiles are known for many years (Sadeghi-Kiakhani, 2015; Mehrparvar et al., 2016; Kalyoncu et al., 2006).

Cochineal (Figure 1 b) is a very popular natural dye in food, cosmetic, pharmaceutical, and textile industries with high consumption (Mirnezhad et al., 2017; Safapour et al., 2019). Cochineal is obtained by crushing the dried bodies of female *coccus cacti* scales, which live in Central America and Mexico. Carminic acid, based on anthraquinone, is the primary coloring agent in Cochineal, and it can produce various colors on the textiles in the presence of inorganic mordants (Valipour et al., 2014; Sadeghi-Kiakhani et al., 2016; Singh and Kumar, 2014).

(a) The main anthraquinones in water: ethanol extract of madder root include (1)

Lucidine premeveroside, (2) Ruberythric acid, (3) Pseudopurpurin, and (4) Munjistine

(Derksen et al., 2003; Willemen et al., 2018)

(b) Carminic acid (Singh and Kumar, 2014)

Figure 1. Chemical structures of compounds extracted from (a) Madder roots and (b)
Cochineal insects

Nowadays, people are more concerned about human health and environmental pollutions resulting from petroleum-based products and heavy metals. For this purpose, the general shortcomings of natural dyes should be overcome. These shortcomings include high cost, low color yield, low shade reproducibility, complex dyeing process, low affinity, and color fastness properties on textile fibers. The latter may be overcome by mordanting using various inorganic salts. The metallic mordants usually improve the dye affinity, color gamut, and colorfastness properties by complexation and form a bridge between natural dyes and fibers. Most of these metals are toxic and can provide severe problems in wastewater treatments after the dyeing process (Bechtold and Mussak, 2009; Kasiri and Safapour, 2014).

One of the aims of wet textile processes is to improve the color strength and color fastness properties of natural dyes on textiles. The overall goal is to simultaneously dye and finish textiles via an environmentally-friendly treatment and reduce a load of pollutants in wastewater and environment (Sadeghi-Kiakhani and Safapour, 2015; Varadarajan and Venkatachalam, 2016). A literature survey showed that researchers had used polysaccharide derivatives as green and sustainable materials for enhancing the dyeability and surface coating of textiles

before (Enescu, 2008, Zhang and Wang, 2015). However, there was no report on using SA-Ag NPs nanoparticles to enhance the dyeability and finishing of wool fibers. In this study, SA-Ag NPs nanoparticles were used to impart green antimicrobial and antioxidant finishing of wool yarn used in the handmade carpet. Also, two natural green dyes, including Madder and Cochineal, were used for the dyeing of the treated samples. The effects of significant parameters on the dyeing process were optimized, and the colorfastness properties of the samples were assessed.

2-Experimental

2.1- Materials and equipment

The bleached wool yarn with specification of 200 Tex/4 fold was purchased from Azar Barf (Iran). Sodium alginate, with a purity of 99.8 %, was obtained from Sigma. Cochineal and Madder dyes (dried powder) were purchased by the local dyeing mills. AgNO₃, with a purity of >99%, was supplied from Merck Co. Sodium hypophosphite, citric acid and all materials utilized were of analytical grade.

SEM-EDX (TESCAN-MIRA3-FEG, Czech Republic) was applied for the investigation of surface properties of the treated yarn. The reflectance spectrophotometer (Color-Eye® X-Rite Inc.) with an illuminant D65 and standard observer 10 degree was used for the determination of Color data of dyed samples. Wool coloration was performed by Smart dyer rapid (India). Ultrasonic extraction was conducted in a double-jacketed cell within a 3L ultrasonic cleaning bath (Sonorex DT/DL/RK100/102(H)-UK). Washing of samples was carried out by a Rotadyer device (Nasaj Sanat Yazd Ltd.).

2.2- Pretreatment of wool with SA-Ag NPs

The washing of wool yarn (1g) was completed by 5 g/L non-ionic soap with L.R. 1:40 at 60 °C for 20 min. Finally, the samples were rinsed and dried at ambient temperature.

The SA-Ag NPs was applied on the wool yarns via a pad-dry-cure method. The aqueous solution of AgNO₃ at a concentration of 0.06 M was ultra-sounded and dissolved in NaOH aqueous solution (0.3 M, 30 mL, pH=8-9) (Aryabadie et al., 2015). Then, SA (0.1, 0.5, 1 and 5% o.w.f.) was added and solubilized at 30 °C. 4% o.w.f. sodium hypophosphite and citric acid were added to the prepared solution at pH=5 as a cross-linker and a catalyst, respectively. Then, wool yarn (1 g) was treated in the prepared solution using an incubator shaker at 60 °C for 3 hours with shaking speed of 120 rpm. The samples were dried (temperature 75 °C, and time 30 min), and then cured (temperature 110 °C, time 3 min). Finally, the samples were rinsed to eliminate the disconnected compounds with fibers. The dried wool samples were weighed before and after the treatment to measure the weight gain (%).

2.3. Dyeing procedure

The dyeing of all samples was performed with Madder and Cochineal natural dyes at various concentrations 5-60 % o.w.f. and 5-40 % o.w.f., respectively. The samples (1 g) were immersed to dyeing bath with L.R. 50:1 at 30 °C. The dyeing temperature was raised to the set temperature (70, 80, or 90 °C) with rating 2 °C/min, and the dyeing process was performed at different time intervals and pHs. Finally, the samples were rinsed, and dried.

The measurement of color strength (K/S) of the dyed wool samples was completed by Kubelka-Munk equation (Eq. 1):

$$K / S = \frac{(1 - R)^2}{2R} \quad \text{Eq. 1} \quad 156$$

Where R is reflectance at the maximum absorption wavelength of the dyed sample, K is the
absorption coefficient, and S is the scattering coefficient of dyed wool yarns. At least three
individual measurements were performed on each sample to report the average value and
satisfy the repeatability and accuracy of the collected data. 160

2.4. Measurements of colorfastness 162

The light-, wash-, and rub- colorfastness properties of the samples were specified by the
standard procedures. The light-fastness was measured following the standard ISO105-B02;
1994 (E) using a xenon lamp, and a blue scale was used to assess the samples. Furthermore,
the wash fastness of dyed wool samples was specified by the ISO105 B01-C2S standard
method. The staining on the adjacent fabrics and color changes of dyed samples were evaluated
by grayscale. The ISO105-X12: 1993 (E) standard was used to measure the fastness to rub of
dyed samples in wet and dry conditions, and was evaluated by grayscale. 169

2.5. Antimicrobial assay 171

The antimicrobial characteristics of all samples were determined by ASTM E2149-01 manner. 172
Briefly, Muller-Hinton broth (10.0 mL) were autoclaved (T 121 °C and t 15 min). 10^6 - 10^7 mL⁻¹
CFU (colony-forming units) of inoculums of bacteria was prepared, and the incubation of all
samples was performed (T 37 °C and t 24 h). Then, the solution (100 µL) of each sample was
added to the agar plate and scattered over it. The samples were incubated (T 37 °C and t 24 h), 176

and lastly, the counting of the colonies on the plate was done (Singh et al., 2005). The reduction
growth of bacteria ($R\%$) was determined by Eq. 2.

$$\% R = \frac{A - B}{A} \times 100 \quad \text{Eq. 2}$$

Where, B is the surviving cells (CFU/mL) for raw wool, and A is the surviving cells (CFU/mL)
for treated samples. All experiments were completed at least three times, and the average
amount for each test was reported.

2.7. Antioxidant measurement

The antioxidant potential of all samples was evaluated by DPPH method (Sellimi et al., 2015).
The wool samples (0.1 g) were immersed in the DPPH methanol solution (0.15 mM, 40 mL).
The samples were incubated at ambient and dark conditions for 30 min. To determine the color
change and absorbance values of each sample at $\lambda_{\text{max}} \sim 517 \text{ nm}$, the UV-visible
spectrophotometer was utilized, and reduction percent ($R\%$) of free radical scavenging of all
samples was calculated by Eq. (3).

$$\% R = \frac{C - D}{C} \times 100 \quad \text{Eq. 3}$$

Where C is the absorbance values of raw and D is absorbance values of treated samples (Sellimi
et al., 2015).

3. Results and Discussion

3.1 Fiber Characterization

3.1.1. Weight gain

The SA-Ag NPs in various concentration was applied on the wool yarns, and the weight gain of samples was presented in Figure 2. The wool samples are treated with SA-Ag NPs, and they bind to the surface by hydrogen, electrostatic or Van der Waals interactions. In the presence of citric acid, the grafting of SA-Ag NPs on the wool fibers can be formed chemically bond with free hydroxyl and amine groups. Figure 2 confirms that the wool fibers is saturated at SA-Ag NPs concentrations above 1 % ow.f. So, the optimum amount of SA-Ag NPs for the treatment of wool fibers to avoid wasting the SA-Ag NPs is considered 1 % ow.f.

Figure 2. The effect of SA-Ag NPs concentration on the weight gain of wool samples

(Conditions: 60 °C, pH 5, L.R=30:1 for 3h)

3.1.2. SEM-EDX analysis

The surface morphologies of wool yarns are given in Figure 3. In SEM micrographs of treated wool fiber, a thin layer of SA-Ag NPs is observable, and looked smoother with some small particles. The EDX analysis confirmed the presence of silver on the treated sample.

Figure 3. SEM micrographs of (a) wool and (b) treated wool; EDX analysis of (c) wool and (d) treated wool, ([SA-Ag NPs]=1% o.w.f., temperature 60 °C, pH 5, L.R=30:1, for 3 h)

3.2. Dyeing properties

3.2.1. Effect of SA-Ag NPs concentration

The dyeing of wool yarns with Cochineal and Madder (30% o.w.f.) was performed at L.R 1:40, T 95 °C, and pH 5 for 60 min. The influence of pretreatment of wool yarns with SA-Ag NPs at various concentrations on the dyeability of the treated wool yarns by natural dyes was presented in Figure 4. The K/S values of the treated wool yarns improved noticeably. The results indicated that the K/S values of untreated wool yarns dyed with Cochineal and Madder

were 2.2, and 12.4, respectively. While, the K/S values of wool samples treated with 1% o.w.f. of SA-Ag NPs dyed with Cochineal and Madder increased to over 7 and 14, respectively. The enhancement can be related to the more attainable dye sites produced on the treated samples (i.e., carboxyl and hydroxyl groups of SA) on the treated wool (Derksen et al., 2003; Sadeghi-Kiakhani and Safapour, 2015). The natural dyes may also bind to the treated wool fibers through complexation with Ag ions. The saturation point of weight gain % vs. SA-Ag NPs concentration and K/S values vs. SA-Ag NPs was at 1% o.w.f., and this value was chosen as an optimized treatment concentration. The addition of more SA-Ag NPs does not seem to increase the number of available dye sites on wool fibers.

Figure 4. Influence of pretreatment of wool yarns with SA-Ag NPs at various concentrations on the dyeability of natural dyes; Madder and Cochineal 30% o.w.f., T 95 °C, pH 5, t= 60 min, L: R 1:40.

3.2.2. Effect of dye concentration

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The different initial dye concentrations of natural dyes were applied on the wool samples, and K/S values of them has been shown in Figure 5. Results indicated different behaviors and the slopes of K/S values for the treated samples. The treated samples were saturated with cochineal and madder at 30% o.w.f. concentration. While no clear saturation point was observed for those of untreated wool yarns. The trends in Figure 5 show that more accessible dye sites are available on the wool treated with SA-Ag NPs compared to those of untreated samples. The trend clearly shows that the grafting of SA-Ag NPs on the wool yarns can lead to dye with Cochineal or Madder at much lower initial concentrations with relatively high color strengths (i.e., K/S values). This trend reduces the amount of dye needed for dyeing and also remaining dye in the wastewater. As a result, considerable amounts of dye and chemicals can be saved in natural dyeing of treated samples with SA-Ag NPs that is important from the ecological and economic points of view (Willemen et al., 2018; Kalyoncu et al., 2006).

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Figure 5. The K/S values of the treated wool samples at various initial dye concentrations of natural dyes; SA-Ag NPs 1% o.w.f., T 95 °C, pH 5, t 60 min , L.R 1:40.

3.2.3. Dyeing duration

Reducing the duration of the dyeing process is another factor that can lower the energy and cost of the whole process. Figure 6 shows that the K/S values slightly increases by prolongation of the dyeing process from 30 min to 60 min and levels off afterward. This trend suggests that the optimum dyeing period can be considered as 60 min for all samples, and enhancing the dyeing process duration does not have any tangible improvements of the K/S values. It should be noted that faster equilibrium may be achieved at elevated temperatures.

Figure 6. The K/S of wool samples at various dyeing process durations; Cochineal and Madder 30% o.w.f., T 80 °C, pH 5, L.R 1:40.

3.2.4. Effect of temperature of dyeing

The treated wool yarns were dyed at 70, 80, and 90 °C for 60 min under the same dyeing conditions (Figure 7). A faster dyeing equilibrium can be achieved at elevated temperatures. However, the absorption of natural dyes on the treated samples at 70 °C are noticeably more than those of the wool yarns dyed at 90 °C. This suggests the possibility of decreasing the dyeing temperature, and such improvement can diminish the consumption of costs and energy in natural dyeing of the wool fibers, which is very favorable (Safapour et al., 2019, Sadeghi-Kiakhani and Safapour, 2015).

Figure 7. The K/S of wool samples at various temperatures of dyeing process. Cochineal and Madder 30% o.w.f., t 60 min, pH 5, L.R 1: 40.

3.2.5. Effect of pH of the dyeing bath

The absorption of natural dyes on the wool fibers is under the influence of pH of the dyeing bath (Derksen et al., 2003). At pH 7, the K/S values of wool samples dyed with Cochineal were noticeably lower than pH 4 (Figure 8). This shows that the absorption process is mainly driven by electrostatic interactions between Cochineal and positively charged wool fibers in acidic pH 4. The $-NH_2$ groups (amino) of wool are activated in acidic medium ($pH < 5$) (Paques et al., 2014; Sun and Tan, 2013). Therefore, the electrostatic interactions take place between cochineal natural dye and wool fiber, which causes to increase the dye absorption on wool. At pH 7, the quantity of $-NH_3^+$ (activated amino groups) decreases, and as a result, the cochineal dye absorption on the wool diminishes. This behavior can also be explained by higher water solubility of carminic acid at pH 6.5 and above due to the deprotonation of its carboxylic group (Figure 1) (Baines and Seal, 2012). The treated wool fibers with SA-Ag NPs also have negative

charges at pH 7 due to activation of the functional groups (hydroxyl and carboxyl) of alginate, and by decreasing the pH, the negative charges of the treated wool fibers is diminished. Thus, the treated wool absorbed higher cochineal dye at pH 4, due to the electrostatic interactions, complex formation, and hydrogen bonding between the treated wool with SA-Ag. The all samples dyed with Madder had similar K/S values to each other at pH 7 and 4. This suggests that the electrostatic interactions are less pronounced in the wool dyeing with Madder dye at various pHs. The reason for such different dyeing behavior between Cochineal and Madder can be described to their different chemical configurations. The percentage of chemical components without carboxylic groups (i.e., Lucidine premeveroside, Ruberythric acid) in the extracted mixture of Madder is probably much higher than the other species with carboxylic groups (Figure 1). Therefore, the major components of Madder in the solution do not have any carboxylic groups to be protonated/deprotonated, and consequently the weak van der Waals forces and hydrogen bonding are effective in wool dyeing with Madder.

Figure 8. The K/S of wool samples at various pHs of dyeing process. Cochineal and Madder 30% o.w.f., T 80 °C, t 60 min, L.R 1:40

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3.3. Colorfastness properties

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The colorfastness properties of dyed samples are given in Table 1. Generally, the fastness of dyed samples to wash and rub are depended on the strength of bonds formed between the dye molecules and fibers. As can be seen from Table 1, the colorfastness properties of the samples were generally very good and were further improved by the pretreatment. The presented results show the presence of strong intermolecular interactions between Madder and Cochineal with wool fibers. The improvement of light-fastness properties from 6-7 to 7-8 is a sign of complex formation between the dyes and treated wool fibers.

Due to the absence of ionic interactions between the main extracted components of Madder with wool fibers, the general fastness properties of wool fibers dyed with Madder are slightly lower than those of Cochineal on wool fibers (Table 1). Cochineal has a carboxylic group, which can improve the dye-fiber interactions via electrostatic interactions.

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Table 1. Colorfastness of wool samples dyed with natural dyes, Cochineal and Madder 30%
o.w.f., T 80 °C, t 60 min; pH 5, L.R 1:40

Dye	SA-Ag NPs %(o.w.f.)	Washing			Light	Rubbing	
		C ^S	N ^S	Ch		Dry	Wet
Madder	-	4	4	4	6-7	3-4	4
	1	4-5	4-5	4-5	7-8	4-5	3-4
	5	4-5	4-5	4-5	7-8	4-5	4
	-	4-5	4-5	4-5	7	4-5	4
Cochineal	1	5	5	5	8	4-5	4-5
	5	5	5	5	8	4-5	4-5

3.4. Colorimetric properties

Table 2 lists the colorimetric data of the dyed samples with Cochineal and Madder. It was observable that the both of K/S and ΔE values were increased by increasing the concentration of SA-Ag NPs in the pretreatment. There were negligible differences between the values for the samples treated at 1% and 5% of SA-Ag NPs.

Table 2. Colorimetric data of dyed samples with natural dyes (SA-Ag NPs 1% o.w.f.,
Cochineal and Madder 30% o.w.f.; T 80 °C, t 60 min, pH 5)

Dye	SA-Ag NPs %(o.w.f.)	L*	a*	b*	C*	h*	K/S	(ΔE)
Madder	0	39.92	24.05	7.25	25.12	16.77	9.01	-
	1	36.26	22.54	13.55	16.30	31.01	14.83	7.44
	5	36.05	23.16	11.24	25.74	25.88	15.02	5.62
Cochineal	0	46.43	21.48	-4.08	21.86	349.24	20.38	-
	1	32.99	19.28	-4.19	19.73	347.73	24.14	13.61
	5	32.40	19.85	-4.23	20.29	347.97	24.27	14.12

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3.5. Antimicrobial activity

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The antimicrobial activity of the wool samples has been provided in Table 3. The untreated wool yarns after dyeing with Madder and Cochineal had antimicrobial activity 20%, and 35%, respectively. This trend shows that both of these natural dyes possess weak antimicrobial activities as mentioned in other papers as well (Bechtold and Mussak, 2009; Baines and Seal, 2012). It was found that SA-Ag NPs can increased to ~ 74% the antimicrobial activity of the wool yarns, and dyeing these samples with Cochineal and Madder further increased the antimicrobial activity to 80-85%. So, SA-Ag NPs were found responsible for the antimicrobial activity of the treated samples (Lee and Mooney, 2012; Singh et al., 2011; Pawar and Edgar, 2012). The acceptable mechanism for inhibition of bacteria by Ag ions in SA-Ag NPs composite may be the linkages of the Ag positive ions with the cell surface of bacteria containing the negative charge, which leads to a wide variety of surface and permeability of the cell. Also, due to the thicker cell wall of *S. aureus* as a gram-positive bacteria, it had the

353

more resistance to wool treated with SA-Ag NPs as compared to *E. coli* (Singh et al., 2011; Zahran et al., 2014).

Table 3. the reduction growth (%) of microbial on wool samples (1% o.w.f. SA-Ag NPs after 5 wash cycles; Cochineal and Madder 30%o.w.f., t 60 min, T 80 °C, pH=7)

Dyes	SA-Ag NPs %(o.w.f.)	Reduction (%)	
		<i>S.aureus</i>	<i>E. coli</i>
	0	-	-
	1	74	77
	5	78	82
	0	15	20
Cochineal	1	85	81
	5	86	82
	0	30	35
Madder	1	89	83
	5	88	81

3.6. Antioxidant property

The antioxidant potential of all samples was measured by the DPPH radical scavenging assay (Figure 9). Due to the scavenging nature of SA-Ag NPs, the antioxidant activity of treated wool enhanced by increasing the concentration of SA-Ag NPs up to 1% o.w.f. (Sellimi et al., 2015; González et al., 2010). The untreated wool sample dyed with Madder did not show any better

results than that of the undyed sample. However, the untreated samples dyed with Cochineal 374 enhanced the antioxidant activity more than 10% (Sadeghi-Kiakhani et al., 2019). In general, 375 the incorporation of silver nanoparticles in SA biopolymer not only could provide antibacterial 376 activity on wool yarns but also has enhanced the preservation against free radicals. Thus, it 377 leads to improve the light fastness of dyed samples, and it could be beneficial in biomedical 378 applications of textiles 379

Figure 9. Antioxidant activity of the wool samples. (Cochineal and Madder 30%o.w.f., t 60 381 min, T 80 °C, pH 5) 382

3.6. The durability of the pretreatment 384

The durability of the treated samples after ten repeated washing cycles was measured (Table 385 4). Due to strong grafting and anchoring of SA-Ag NPs on wool fibers, the treated samples 386 demonstrated a very good durability (>70%) even after ten washing cycles. The SA-Ag NPs 387 can separate from the surface of wool fibers during dyeing or washing, which adversely affect 388

the antimicrobial and antioxidant activities. The durability of such treatment would be much lower in the absence of citric acid as mentioned elsewhere (Dastjerdi et al., 2009).

Table 4. The durability of the treated samples after repeated washing cycles (SA-Ag NPs 1% o.w.f., Cochineal and Madder 30%o.w.f., t 60 min, T 80 °C, pH=5)

Repeated Washing Cycles	Dye (%o.w.f.)	Antibacterial activity (%)		Antioxidant activity (%)
		<i>E. coli</i>	<i>S. aureus</i>	
-	-	100	100	74
	Madder	83	89	77
	Cochineal	81	85	89
5	-	98	97	71
	Madder	79	83	72
	Cochineal	76	80	83
10	-	95	92	69
	Madder	77	80	70
	Cochineal	73	77	80

4. Conclusion

The pretreatment of wool yarns with bio-based SA-Ag NPs enhanced their dyeability, antimicrobial, and antioxidant properties. Results indicated that the available dye sites on the treated samples with SA-Ag NPs was increased, and consequently, the strength of intermolecular interactions between the Madder and Cochineal natural dyes and wool fibers was enhanced. The pretreatment of wool yarns with SA-Ag NPs increased the antimicrobial

and antioxidant efficiency above 70%. The colorfastness properties were also slightly improved, probably due to better intermolecular interactions and complex formation with the natural dyes. This environmentally-friendly method can be used for improving the absorption of natural dyes on the wool fibers, reducing the amount of dye needed to obtain the same K/S value at a lower dyeing temperature and a shorter dyeing time. Moreover, the antimicrobial and antioxidants properties of such treatment remained above 70% even after ten repeated washing cycles. The proposed pretreatment is a promising wool finishing process that can be scaled-up easily in the textile industry.

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