Application of Silver Nanoparticles as an Antibacterial Mordant in Wool Natural Dyeing: Synthesis, Antibacterial Activity, and Color Characteristics

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Abstract: Madder is a natural colorant which is commonly applied with metal salts as a mordant to improve its affinity to fibers and color fastness. Madder produces an insoluble complex or lake in the presence of metal ions on mordanted fabric. In this study, wool fabric was pretreated with AgNPs (silver nanoparticles) as a mordant, then dyed with madder. The wool fabric samples were examined by scanning electron microscopy (SEM) and their colorimetric characteristics were evaluated. The formation of spherical silver nanoparticle was confirmed using UV-Visible spectroscopy, SEM images, and elemental analysis. The average size of synthesized silver nanoparticles on the surface of wool fibers is around 73 nm. The dyed wool samples were pretreated with different concentration of $Ag⁺$ ions or AgNPs, which showed higher color strength value compared to untreated dyed wool fabric. This pretreatment also presented good antibacterial activity.

Keywords: Natural dye, Extract solution, Alizarin, AgNPs

Introduction

Wool is a natural protein fiber and is a good media for growing different microorganisms. Therefore, treating with efficient antibacterial agents is required by international standards through certification [1]. Silver both in ionic and nanoparticle form as well as their-based compounds are well-known as an antibacterial agent and are highly toxic to micro-organisms. Silver salt is generally used to provide the needed antibacterial effect, but when silver nanoparticles are used, there is a huge increase in the surface area available for the microbe to be exposed [2]. Silver nanoparticles compared to silver ions are increasingly used due to their slower dissolution rate, leading to a continuous release of silver ions [3]. Moreover, comparing the biological effects of ionic and nanoparticle forms of silver has generated a high interest in using silver nanoparticles in consumer products and medical products [4].

Literature has depicted many ways to synthesize silver nanoparticles, which include physical, chemical, and biological methods. From a practical point of view, chemical reduction from aqueous solutions is the preferred approach to the obtaining nano-sized silver particles because of its simple performance and mild conditions [5]. Thus, nanoparticle preparation relies on chemical reduction of metal salts. Generally, $AgNO_3$ is used as a salt precursor [6], and the reducing agent is a chemical material that can be made up of any one of many choices such as polyols, sodium borohydride, hydrazine, sodium citrate, and N, N-dimethylformamide [7]. Nowadays, there is a growing interest in developing ecofriendly processes. Therefore, researchers have turned to biological reducing agents for synthesis of silver nanoparticles [8-13]. Generally, natural reducing agents have a low redox potential and are more time consuming when used in biological methods compared to chemical methods [7,14]. Aqueous extracts from natural colorants are the preferred reducing agents for the biosynthesis of silver nanoparticles [15].

Natural colorants have been used since ancient times in various applications and they are being reintroduced for use due to growing attention on the harmful effects of synthetics dyes. Natural colorants are usually obtained from animals (insects) or vegetable such as roots, stems, barks, leaves, berries and flowers without chemical processing [16-18]. Natural colorants are mainly mordant dyes and usually have weak dye fastness when applied on fabrics. It is common to improve their affinity to substrate or color fastness by applying metal salts as a mordant [19].

Madder is a well-known natural dye which produces an insoluble complex or lake in the presence of metal ions on mordanted fabric. In the current study, wool fabric was pretreated with silver in the form of ionic (Ag^+) or nanoparticles (AgNPs), then dyed with madder as a natural colorant. The madder roots contain several polyphenolic compounds that can reduce silver ions to AgNPs [20]. The pretreated wool fabric samples were examined by scanning electron microscopy (SEM) and their colorimetric characteristics was evaluated. Moreover, the antibacterial property of samples was examined and reported.

Experimental

Chemical Agents

All chemical agents used in this study were analytical grade and distilled water was used throughout the experiments. *Corresponding author: barani@birjand.ac.ir Silver nitrate (AgNO₃ extra pure, > 99.8%) was used as a

precursor of silver nanoparticles, along with sodium borohydride (NaBH4, 99.9 %) as a reducing agent, and acetic acid $(CH₃COOH, 99.7%)$ for adjusting the pH were purchased from Merck Co (Germany). The Madder, Rubiatinctorum L., as a natural dye was prepared from the Yazd province, Iran.

Wool Fabric

The wool fabric samples were supplied by Iran Merinos Co. (Iran). The characteristics of the wool fabric are presented in Table 1. First, the wool fabric samples were cleaned from impurities and immersed in a solution containing 1 g/l nonionic detergent (Triton X100), for 30 min at 50° C, then rinsed with tap water and dried at 25° C.

Synthesis of Silver Nanoparticles

The scoured wool fabric was immersed in different concentrations of silver nitrate solution (Table 2) with a material-to-liquor ratio of 1:40 for 1 h at 25 °C. After that, half of the pretreated fabric was immersed in sodium borohydride solution as a reducing agent with a material-toliquor ratio of 1:60 for 20 min at 25° C. This step was done at low temperature to prevent reaction of sodium borohydride with water at high temperatures which can take place and form the following [21].

$$
NaBH4 + 4H2O \longrightarrow NaB(OH)4 + 4H2
$$
 (1)

The reducing agent concentration was adjusted to twice the concentration of silver ions, to guarantee the total $Ag⁺$ in wool fabric is reduced to Ag atoms (equation (2)). In addition, high concentration of reducing agent resulted in high nuclei, which led to smaller AgNPs [22]. The color of wool fabric was altered to brown which confirms the synthesis of silver nanoparticles in the wool fiber [23].

Table 1. Characteristics of wool fabric samples

Weight	Warp	Weft		Yarn
area	density	density		fineness
(g/m^2)		$(count/cm)$ $(count/cm)$		(Nm)
262	20		Plain structure	48/2

Table 2. Sample code and characteristics of treated wool fabric with silver nanoparticles

$$
AgNO3 + NaBH4 \longrightarrow Ag* + 1/2H2 + 1/2B2H6 + NaNO3
$$
\n(2)

The pretreated wool fabrics were rinsed with distilled water and dried in oven at 80 °C for 20 min and dyed with madder as natural colorants. The other half of pretreated wool fabrics with Ag⁺ were immediately dyed with madder without sodium borohydride solution treatment.

Dyeing Procedure

To extract the dyestuff from madder, the well-milled parts of madder roots were boiled in distilled water for 60 minutes while stirring simultaneously. The extract solution was cooled to room temperature and filtered, then the volume solution was adjusted with distilled water to obtain 10 wt % of dye solution. The dyeing process was carried out using the extracted madder solution (100 % on weight of fabric sample) and the pH of dyeing bath solution, which was adjusted to 5.5 using acetic acid. The liquor-to-goods ratio was adjusted to 40:1. The pretreated wool fabric samples were introduced to the dyeing bath solution at around 50° C. The temperature was raised gradually to boiling point with a gradient of 2 °C/min, and followed at this temperature for 1 h.

Characterization of Silver Pre-treated Wool Fabric

Surface morphology of pretreated wool fabrics was observed by SEM (Zeiss, Merlin Series). This microscope was equipped with energy dispersive X-ray spectroscopy (EDS). First, wool fabric samples were coated with a gold layer and then observed by SEM. The average diameter of silver nanoparticles (AgNPs) was determined using Digimizer 4.1.1.0 software, and the mean value for 20 measurements was reported. The UV-Vis absorption spectra of fabrics were taken by a Thermo Scientific Evolution 220 UV-Visible spectrophotometer with an ISA-220 integrating sphere accessory. Moreover, the pretreated wool fabrics were well cut and soaked in distilled water at room temperature for 24 h. Then, as a comparison the UV-Vis absorption spectra of the extracted solution of AgNP-pretreated wool fabric was taken at room temperature on an OPTIZEN 2120 UV spectrophotometer.

The Shimadzu IRAffinity-1 FTIR instrument (Nakagyoku, Kyoto, Japan) was used to analyze to find out the effect of silver nanoparticles treatment as mordant on the chemical functional groups of wool sample. Resolution for the infrared spectra was 4 cm⁻¹. A film of wool powder and KBr pellets was prepared and its infrared absorbance was collected from 400 to 2000 cm^{-1} .

Color Measurement

The reflectance spectra of wool fabric samples was measured with X-Rite Gretag Macbeth Color Eye 7000A benchtop sphere spectrophotometer (X-Rite, Inc. Grand

Rapids, MI, USA) in the range 360-740 nm. The CIE terms namely, L^*, a^*, b^* , and C^* color coordinates under illuminate D_{65} and a 10[°] standard observer was measured for evaluating the color of samples. The color strength of samples was calculated as follows:

$$
\frac{K}{S} = \frac{(1-R)^2}{2R} \tag{3}
$$

where R is the reflectance of the sample, K is the absorption coefficient, and S is the scattering coefficient.

The percentage of relative color strength (K/S) of each dyed fabric was measured from the reflectance value of the dyed sample at each wavelength by equation (4). It describes the ratio based on the $(K/S$ -value) of the sample in relation to the $(K/S$ -value) of the standard and is expressed as a percentage.

Relative strength (%) =
$$
100 \times \frac{\sum_{360}^{740} (K/S) trial}{\sum_{360}^{740} (K/S) std}
$$
 (4)

Moreover, the hue angle (h) which is the angular component of the polar representation was determined according to the following equation;

$$
h = \text{Arc tan} \left(b^* / a^* \right) \tag{5}
$$

Pretreatment of wool fabric samples with AgNP results in a color change of sample to brownish yellow [23] and is described by a yellowness index. The yellowness index (YI) of wool fabric samples was calculated according to the ASTM E313.

The color fastness of dyed wool samples was tested per the ISO 105-CO2:1989 standard test method.

Antibacterial Properties

The antibacterial property of wool fabric samples against Staphylococcus aureus, a gram-positive bacteria, was carried out per a modified version of the Parallel Streak AATCC 147-2004 test method. The test is also known as an agar diffusion method based on an inhibition zone surrounding the sample, where bacteria growth is inhibited on the inoculated agar plate. First, specimens were prepared with a diameter of 1.6 mm. Each surface of preloaded petri dishes with 25 ml of nutrient agar was seeded individually with a fresh bacterial suspension (10^8 CFU/ml) by a sterile cotton swab using the four-zone method. The prepared sample was gently placed on the inoculated agar plate. The petri dishes were incubated for 24 h at 37° C. In the following, the diameter of inhibition zone was determined and reported. The average width of the inhibition zone for each specimen was calculated as follows:

$$
W = \frac{(T - D)}{2} \tag{6}
$$

where W is the width of the inhibition zone and T is the total diameter of the test specimen and its clear zone. D is the diameter of the test specimen in mm.

Results and Discussion

UV-Vis Spectroscopy Results

Optical absorption spectrum is a technique that helps to characterize the structure of metal nanoparticles. In noble metals, a size decrease that goes below the electron free path gives rise to intense absorption in the visible-near-UV [24]. The extinction spectra are very sensitive to the shape, size, size distribution of nanoparticles, stabilizer and refractive index of media [25]. The UV-Vis absorption spectrum of treated wool fabric samples with or without sodium borohydride is presented in Figure 1(a). The presence of an extinction peak near 440 nm on AgNP-pretreated wool fabric sample was confirmed the synthesis of spherical shaped AgNPs [22,26]. In addition, the UV-Vis absorption spectrum of extract solution from AgNP-pretreated and untreated wool fabric is presented in Figure 1(b). A single extinction peak was formed in all samples as well as in the extract solution of a madder dyed wool sample, which was

Figure 1. UV-Vis absorption spectrum of (a) pretreated wool fabric samples with silver ions (Ag400) and AgNPs (AgN400) and (b) extract solution of treated and dyed wool fabric.

Figure 2. The deconvoluted absorption spectra of extract solution of (a) dyed wool sample without pretreating with silver and (b) dyed wool sample pretreated with AgNPs.

not pretreated with Ag^+ or AgNPs. The latter extinction peak of around 410 nm was due to the release of madder dyed wool extract solution's chemical coloring constituents [27]. The extract solution of AgNP-pretreated wool sample presented an extinction peak at a similar position in the madder solution, but with a higher intensity due to the presence of AgNPs, which enhanced the intensity of this peak. The deconvoluted absorption spectra of the extract solution of AgNP-pretreated and untreated wool fabric samples are shown in Figure 2. Pretreating a wool fabric sample with AgNPs caused a new extinction peak to appear that was around 397 nm, which confirmed the presence of silver nanoparticles in a wool fabric structure. Moreover, the synthesized silver nanoparticles had a spherical shape which was evident in the single extinction peak [28].

Synthesis of the Silver Nanoparticles Mechanism

Wool fibers are able to bind with opposite charged organic or inorganic molecules due to their polar and ionizable groups [29]. The carboxyl group (-COOH) on the amino acids and hydroxyl group (OH) on the madder dye molecule are the most binding sites that can bind to positive charge molecules [30]. Silver ions (Ag^+) can diffuse or absorbe due to electrostatic interaction and then are converted to silver atoms (Ag). Absorbed silver ions on the pretreated wool fibers were reduced to silver atoms when faced with the sodium borohydride solution, which is a strong reducing agent. Sodium borohydride yields a very quick reduction of silver ions. The primary AgNPs coalesced with each other and formed large nanoparticles that are also known as secondary nanoparticles. The silver atom clustered and created nanoparticles. Therefore, the color of wool fabric was altered to a brown color, which confirms the formation of silver nanoparticles in the wool fiber structure [23].

In the case of Ag⁺ pretreated wool fabric, the extracted dyestuff solution of madder as a natural colorant can act as a reducing agent. One of the main chemical coloring constituents of madder is alizarin, rubiadin, and purpurin [31,32].

Figure 3. Alizarin (1,2-dihydroxy anthraquinone) is one of the main chemical components, which make up the coloring constituent of madder.

Madder is natural colorant, which produces an insoluble complex or lake with metal ions on fabric. Metal ions are capable of forming a bridge between the functional groups of the dye and the wool protein and lead to a higher dye exhaustion. The metal ions also enhance fastness [33]. The alizarin has two hydroxyl groups in the ortho position in its phenolic ring (Figure 3). The oxygen in a polar group has a strong affinity for silver ions and silver nanoparticles [34]. The first stage involves the formation of coordinative bonding between the oxygen of a hydroxyl group in madder extract and silver ion. Then, these silver ions can be converted to AgNPs with O-hydroxy phenol. They are weak reducing agents, and their reactions will take place slowly, but the dyeing procedure at high temperature $(90^{\circ}C)$ enhances its effect.

Surface Morphology and Elemental Analysis Results

The morphological features of the AgNP-pretreated wool fabric with two different methods at 400 ppm concentration was studied with the use of SEM. Figure 4(a) shows the SEM images of the madder dyed wool fabric sample that was pretreated with Ag^+ , and the highly magnified inset images (Figure 4(a)) also shows the synthesized AgNPs to be an average size of 375 nm. The madder roots contain several polyphenolic compounds able to reduce silver ions to AgNPs. Different reducing agents with different redox

Figure 4. The morphological features of wool fibers that are pretreated with (a) silver ions (Ag400) and (b) AgNPs (AgN400).

Figure 5. Mechanism of AgNPs synthesis in the presence of alizarin.

potential could cause the synthesis of AgNPs in different sizes [15]. Polyphenolic compounds are weak reducing agents, and their reaction takes place slowly, resulting in larger nanoparticles. Therefore, alizarin is the most important polyphenol acting as a reducing agent in AgNP synthesis.

Figure 4(b) depicts the SEM images of a madder dyed wool fabric sample that was pretreated with AgNPs. The highly magnified inset images (Figure 4(b)) show synthesized AgNPs to be an average size of 73 nm. The $Ag⁺$ is first reduced to atoms by means of sodium borohydride. The obtained atoms then nucleate in small clusters and grow into particles. This depends on the availability of atoms, which in turn depends on the silver salt needed to make up the reducing agent concentration ratio, whereby the size and shape of the nanoparticles be controlled. Therefore, the strong reducing agents such as sodium borohydride resulted in a small mono disperse of AgNPs [35]. A tentative mechanism of AgNP synthesis in the presence of alizarin is illustrated in Figure 5.

The elemental analysis of synthesized AgNPs on wool fabrics was performed using the energy dispersive spectroscopy (EDS) on the SEM. Figure 6 shows the EDS spectrum of treated wool fabric samples. The EDS spectrum of the AgNP-pretreated wool fabric clearly showed the presence of silver elements on the surface of pretreated wool fabric. The carbon, nitrogen, oxygen and sulphur peaks are attributed to the wool fiber components. The presence of Au (gold) in the EDS spectra is related to a gold layer, which has been coated on the surface of wool fiber samples to prepare them for SEM images.

FTIR Spectra Analysis of Wool Fibers

The FTIR spectra of untreated wool, AgNP-pretreated wool, and dyed wool samples are presented in Figure 7. To compare the FTIR spectra, they were baseline corrected and normalized on the amide I vibration at 1644 cm⁻¹ [36]. After that, the spectral features were compared in a relative manner. The main characteristic peaks of wool fibers appeared between 1000 and 1700 cm⁻¹, which are related to amide I (1644 cm⁻¹), amide II (1516 cm⁻¹), and amide III (1235 cm^{-1}) [37]. Moreover, a broad band is centered at 3432 cm⁻¹ due to the N-H stretching vibrations of terminal amino group. As can be seen, the dyed wool fiber structure was the same as untreated wool, while a characteristic peak of alizarin appeared at 1456 cm^{-1} [38], and the intensity of

Figure 6. The EDS spectrum of synthesized AgNPs on wool fabrics pretreated with (a) silver ions (Ag400) and (b) AgNPs (AgN400).

Figure 7. FTIR spectra of (a) untreated wool fibers, (b) dyed wool fibers with madder, and (c) AgNP-treated wool fibers.

the band at 3432 cm^{-1} decreased. These changes are due to interaction between the OH of anthraquinone of madder dye and the amide bond of the wool. The AgNP-pretreated wool spectra are similar to those of untreated wool. The peaks associated with amide I, II, and III bands appeared very similar to those for untreated wool. Compared to the untreated wool fiber structure, the peak at 3432 cm^{-1} of AgNP-pretreated wool fiber is much narrower and of lower intensity [39], which is due to interaction of AgNPs with the amide groups.

Colorimetric Characteristics of Dyed Wool Samples

The color strength (K/S) spectra of dyed wool samples, which were pretreated with different concentrations of Ag^+ or AgNPs are given in Figure 8. The untreated wool fabric presented a lower color strength at all visible wavelengths compared to all pretreated wool fabrics. Pretreating wool fabrics with $Ag⁺$ or AgNPs created more functional groups than with untreated wool fabric. Therefore, more reactive sites are available on pretreated wool fabrics that can attach to dye molecules as well as improve color strength [40]. The pretreated wool fabrics with AgNPs showed higher color

Figure 8. Color strength (K/S) spectra of wool fabric dyed with madder while pretreated with different concentrations of $Ag⁺$ and AgNPs.

strength compared to pretreated wool fabrics with $Ag⁺$ at the same concentration. It is reported [41] that AgNPs have a unique localized surface plasmon resonance property and exhibit brilliant colors. The excitation of plasmon by light results in colored colloids containing AgNPs. The colors can be tuned from yellow to red or blue depending on the size, shape, and dielectric properties of AgNPs. Recently AgNPs have been applied as a coloring agent to develop novel hues on wool materials. This method of coloring wool is interesting because the color of wool fabrics can be altered depending upon the morphology of AgNPs [42]. Therefore, it seems that loaded AgNPs on wool fabric forms a red color which enhances the color strength of madder. Moreover, it can be observed that the color strength values of dyed wool fabric increases with an increase of $Ag⁺$ or AgNP concentration which is in agreement with [43].

The colorimetric data of all dyed wool samples with and without silver salts are presented in Table 3. Lightness (L^*) is an important parameter of dyed sample and depends on the surface lustre and specular reflectance of dyed sample. Pretreating wool fabric samples with Ag⁺ or AgNPs resulted

Table 3. The colorimetric data $(L^*, a^*, b^*, C^*$ and $h^*)$ for the dyed samples with and without silver salts

ID	\overline{L}^*	α	b^*	Hue	Chroma	Relative color strength	Yellowness index
Untreated	38.41	28.72	25.55	41.67	38.44	100	27.5
Ag 400	31.10	23.3	22.08	43.48	32.10	152	27.5
Ag200	32.92	23.97	22.29	42.94	32.73	131	27.5
Ag 100	37.65	27.5	24.66	41.91	36.94	104	27.5
AgN400	30.23	14.99	16.6	47.94	22.37	169	38.3
AgN200	34.35	24.63	23.3	43.43	33.91	140	33.2
AgN100	35.93	28.53	25.76	42.10	38.44	111	30.5

Sample	Wash fastness	Staining on cotton	Staining on wool
Untreated		$4 - 5$	$4 - 5$
Ag 400	4	$4 - 5$	$4 - 5$
AgN400	4-5		4-5

Table 4. Wash fastness evaluation of dyed wool fabric with madder

in a low lightness value, which can be due to the lower specular reflectance. It is reported that using metallic salts as a mordant has a significant effect on the shade lightness of dyed fabric with madder [44]. The sample pretreated with the highest concentration (AgN400) of AgNPs presented the lowest brightness value because it had the lowest specular reflectance value. Moreover, pretreating with $Ag⁺$ or AgNPs failed to have significant effect on the shade of dyed sample, except when the sample was pretreated with the highest concentration of AgNPs. But, pretreatment has a significant effect on the chroma value of dyed wool samples and AgN400 sample presented the lowest value. Moreover, the relative color strength of pretreated wool fabric samples significantly increased, which can be due to the yellow brownish color appearing on the pretreated wool sample due to synthesis of AgNPs.

Fastness Assessment

The wash fastness results of dyed wool samples are presented in Table 4. The wash fastness of madder-dyed wool fabric was not improved when treated with silver salt, which might be due to the solubility and release of silver ions [3] while the madder dyed wool fabric sample that was treated with AgNPs presented a good wash fastness due to the formation of an insoluble complex.

Antibacterial Test Results

The antibacterial property of pretreated wool samples with silver salt or AgNPs was analyzed against gram-positive bacteria. The pretreated wool samples with \overrightarrow{Ag}^+ or AgNPs presented an inhibition zone around the dyed sample (Figure 9), while the untreated wool sample that only dyed with madder did not reveal antibacterial properties. The average width of an inhibition zone is presented in Table 5. All pretreated and dyed wool fabric with madder was presented in an inhibition zone compared to untreated wool fabric. Moreover, pretreated wool fabrics with silver salt had a larger inhibition zone compared to AgNP-pretreated wool fabrics. It might be that all loaded silver ions could not reduce to silver atoms due to the lower redox potential of madder colorants' polyphenolic compounds. Therefore, the presence of silver ions created a better release compared to the AgNP pretreated wool samples and provided a larger inhibition zone. In addition, the pretreated wool sample with a high concentration of silver salt had a larger inhibition zone because the antibacterial activity of AgNP nanoparticles

Figure 9. Wool fabric swatches overlaid with Staphylococcus aureus on agar plates: (a) pretreated with different concentration of silver ions (400, 200, and 100 ppm) and (b) pretreated with different concentrations of AgNPs (400, 200, 100, and 0 ppm).

Table 5. The average width of inhibition zone of pretreated wool fabric was dyed with madder

	Control AgNPs concentration (ppm) $Ag+$ concentration (ppm)					
sample	400	200	100	400	200	100
\sim 100 μ	1.5		07	2.5	$\overline{}$	07

depended on its concentration [45].

Conclusion

Size decrease in noble metal particles to the electron free path gives rise to intense absorption in the visible-near/UV range. Therefore, for pretreated wool fabric samples with silver salt, a single extinction peak of around 410 nm at the UV-Vis absorption spectrum was confirmed in the formation of silver nanoparticles. Moreover, the synthesized silver nanoparticles had a spherical shape and presented a single extinction peak. The SEM images of madder dyed wool fabric samples pretreated with \overrightarrow{Ag}^+ or AgNPs confirmed the formation of nanopaticles at an average size of 375 nm and 73 nm, respectively. In addition, the EDS spectrum of the pretreated wool fabric clearly showed the presence of silver elements on the surface of wool fibers.

Pretreating wool fabrics with $Ag⁺$ or AgNPs created more functional groups than with untreated wool fabric. Therefore, pretreatment can provide more reactive sites on wool fabrics and can attach to dye molecules and improve color strength at the same time. The wool fabrics pretreated with AgNPs showed higher color strength compared to pretreated wool fabric with $Ag⁺$ at the same concentration. Moreover, an increase of $Ag⁺$ or AgNP concentration resulted in higher color strength but a lower lightness value compared to untreated wool fabric. All pretreated wool samples with Ag⁺ or AgNPs presented antibacterial activity against Staphylococcus aureus as a gram-positive bacteria.

In conclusion, AgNPs were successfully synthesized on the wool fiber structure and proved capable of forming a bridge between the functional groups of the dye and the wool protein that led to high dye exhaustion and effective antibacterial activity.

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