Journal of Inorganic and Organometallic Polymers and Materials (2020) 30:1153–1161
https://doi.org/10.1007/s10904-019-01335-5

Simultaneous Synthesis of Silver Nanoparticles and Natural Indigo Dyeing of Wool Fiber

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Received: 7 May 2019 / Accepted: 21 September 2019 / Published online: 30 September 2019

Abstract

The wool fiber is a suitable medium for growing different microorganism. In recent years, the treatment of textiles with silver compounds as an active antibacterial agent has gained increased attention to produce advanced medical and hygiene textiles. The current work aims to synthesize silver nanoparticles through two different methods, which are silver pre-treatment and simultaneous silver treatment during indigo dyeing procedures. The formation of spherical silver nanoparticle confirmed by the appearance of a single symmetric extinction peak around 415 nm. The morphology of the indigo-dyed wool fabrics examined using scanning electron microscopy, and their colorimetric characteristics evaluated. The SEM images of wool fiber samples indicated that the silver pre-treatment method resulted in the formation of smaller micro-size (0.73 µm) platelet-like structure of indigo colorant compared with simultaneous silver treatment method (1.46 µm). The indigo-dyed wool samples without silver treatment presented lower color strength at all visible wavelengths compared with silver treatment indigo-dyed samples. Moreover, the simultaneous silver treatment method resulted in a lower color strength compare with the silver pre-treatment method, which due to lower silver content.

Keywords Natural dyeing · Indigo · Color strength · AgNPs · Blue shade

1 Introduction

Wool fiber is a superior natural textile fiber and still extremely demanded by the most consumer due to softness, resilience, breathability, and comfortable attributes [1]. Although, the natural wool fibers come with more or less major deficiencies such as natural hydrophobicity, surface roughness, and good media for the growth and propagation of bacteria under appropriate temperature and humidity. There is a concern that wool can act as a good host for microbe propagation because of its protein nutrient source for bacteria which results in fiber damage and even skin irritation [2]. In recent years, the treatment of natural fibers with efficient antibacterial agents has gained increased attention for producing advanced medical, protective and, hygiene textiles [3, 4]. Therefore, different antibacterial materials such as organic [5] or inorganic compound [6–8] developed for all the types of natural textile material.

Silver compounds are a well-known antibacterial agent compare with some organic antibacterial compounds and represent a good alternative for providing new bioactivity mechanisms [9]. Diffusing silver nanoparticles (AgNPs) into the bacterial membrane cause changes in structural constituents and thus damage the bacterial membrane. Therefore, the permeability of the membrane increases and finally leading to cell death [10]. Several methods reported for the synthesis of AgNPs [4, 11–13], which are including physical, chemical, and biological methods. From a practical point of view, a chemical reduction is a preferred approach for obtaining AgNPs with a easy performance and moderate conditions [14]. Silver metal salt as a precursor with reducing agents as essential compounds used in a chemical reduction method. Also, due to the high surface energy of nanoparticles, it is required to use a capping agent such as surfactant or polymer for coating nanoparticle to prevent from agglomeration [15]. The fibrous textiles, recently have attracted especial attention as soft templates as a capping agents for synthesizing AgNPs at in situ method as well as simultaneously or beside other processes [16].

Indigo colorant as the oldest natural blue dyestuff (C.I. Natural Blue 1), obtained from various plant sources such

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as *Indigofera*, *Polygonum tinctorium*, and *Isatis tinctoria* (Woad) [17]. This plant contains a glucoside structure and knows as an Indicant. This compound hydrolyzes into soluble glucose during the fermentation process, then the colorless indoxyl transforms into blue indigotin (indigo blue) after oxidation process [18]. The indigo as a water-insoluble pigment requires to solubilize with an alkaline reduction in the presence of sodium dithionite [19]. After chemical reduction, indigo becomes water-soluble with high affinity to the wool fibers. To complete the dyeing process and stabilize the dye molecule into the fiber structure, the solubilized dye molecules should return to its insoluble form. For this purpose, the solubilized dye molecules should oxidize to the water-insoluble form of indigo dye molecules [20]. During this process, the insoluble indigo dye particles entrapped inside the wool fiber structure, and thus the dye fastness increases.

In the current study, during the indigo dyeing process which is a alkaline condition, silver ions reduced to the silver nanoparticle in the presence of sodium dithionite which usually uses for the reduction of water-insoluble indigo blue pigment. Therefore, the possibility of AgNPs synthesis examined during the indigo dyeing process through two different treatment methods, which are silver pre-treatment before the indigo-dyeing process, and the other method is the simultaneous silver treatment during the indigo-dyeing process. The morphology of the indigo-dyed wool fabrics examined using scanning electron microscopy (SEM), and their colorimetric characteristics evaluated.

2 Materials and Methods

2.1 Materials

The plain wool fabric sample (weight area 262 g/m^2 and yarn fineness 48/2 Nm) was provided by Iran Merinos Co. (Iran). Prior to the dyeing process, the samples cleaned from impurities by immersing in a solution containing 1 g/L nonionic detergent (Triton X100) at 50 °C. Then, followed for 30 min, and rinsed with distilled water and dried at 25 °C. An analytical grade of silver nitrate ($AgNO_3$ extra pure, $>99.8\%$) as a precursor of silver nanoparticles, sodium dithionite ($Na_2S_2O_4$) as a reducing agent, and ammonia (NH_3) for adjusting the pH value, purchased from Merck Co. (Germany). In this study, the all aqueous samples were prepared with distilled water throughout the experiments.

2.2 Synthesis of Silver Nanoparticles

AgNPs synthesized on the surface of wool fibers using two different methods, including silver pre-treatment and simultaneous silver treatment during indigo-dyeing procedures. In the silver pre-treatment method, firstly the scoured wool fabric immersed in silver nitrate solution (200 ppm) at 25 °C and followed for 40 min. After that, the silver pre-treated wool fabric dyed with indigo colorant according to the recipe in Table 1. In the simultaneous silver treatment method, the silver salt added into the indigo-dyeing bath solution and its concentration adjusted at 200 ppm.

2.3 Dyeing Procedure with Indigo Colorant

Indigo colorant as a natural vat dye is not soluble in water. Thus, before the dyeing process, it is necessary to apply a pre-treatment to prepare water-soluble *leuco*. This pre-treatment procedure carried out at the alkaline conditions in the presence of reducing agents. For this purpose, the indigo colorant solubilized in the presence of sodium dithionite ($Na_2S_2O_4$) and ammonia. After that, a yellow–green solution obtained, which is suitable for dyeing procedure. The dyeing of wool fabric samples with indigo colorant carried out as follows. As mentioned before, sodium dithionite, ammonia, and the indigo dye solution were prepared and mixed at the appropriate liquor ratio according to the reported dyeing recipe in Table 1. The wool fabric immersed to dye bath (20:1 liquor ratio), and the temperature of the dyeing bath was raised to 40 °C, and dyeing procedure followed for 50 min. Then, the sample removed from the dye bath and the soluble form oxidized into the insoluble state. The oxidation method performed by aeration of samples in ambient air for 20 min. All samples washed with nonionic detergent 1 g/L at 40 °C for 10 min, and then the samples rinsed thoroughly with distilled water and dried at room temperature.

Table 1 Dyeing recipe formulation and the sample code of indigo-dyed wool samples

Sample code	Silver salt (ppm)	Indigo solution (OWF, %)	Treating method with silver salt
SIAg0	200	0	Simultaneous treatment
SIAg1	200	1	
SIAg3	200	3	
SIAg6	200	6	
PAgI0	200	0	Pre-treatment
PAgI1	200	1	
PAgI3	200	3	
PAgI6	200	6	
Indigo1	0	1	Un-treated
Indigo3	0	3	
Indigo6	0	6	

In the all above recipe the $Na_2S_2O_4$ (2%, OWF), and ammonia (3%, OWF) was used

2.4 Characterization of Dyed Wool Fabric

The UV–Vis absorption spectra of indigo-dyed fabrics taken by a Thermo Scientific Evolution 220 UV–Visible Spectrophotometer with ISA-220 Integrating Sphere Accessory. Besides, the UV–Vis absorption spectra of an aqueous extracted solution of the indigo-dyed sample measured. Therefore, the dyed wool fabrics well cut to small pieces. They were soaked in a distilled water at room temperature for 24 h. After that, the UV–Vis absorption spectra of an extracted solution of indigo-dyed wool fabrics taken at room temperature by a UV spectrophotometer (Optizen2120UV).

The surface morphology of indigo-dyed wool fabrics were observed by scanning electron microscopy (SEM) (Zeiss, Merlin Series), which was equipped with energy dispersive X-ray spectroscopy (EDS). Before analysis, wool fabric samples sputtered with a thin layer of gold.

2.5 Color Characteristic Measurement of Dyed Wool Fabric

The reflectance spectra of dyed wool fabric samples measured by Color Eye 7000 A, Gretag-Macbeth in the range 360–740 nm. The CIE terms namely, L*, a*, b* and C* color coordinates under illuminate D_{65} and 10° standard observer were measured for evaluating the color of samples. The color strength of the samples calculated according to Eq. 1:

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

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

Hue angle was calculated according to the following Eq. (2) [21];

$$Hue = \begin{cases} ArcTan\left(\frac{b}{a}\right) & \text{for } a \text{ and } b > 0 \\ 180 + ArcTan\left(\frac{b}{a}\right) & \text{for } a < 0 \text{ and } b > 0 \\ 180 + ArcTan\left(\frac{b}{a}\right) & \text{for } a < 0 \text{ and } b < 0 \\ 360 + ArcTan\left(\frac{b}{a}\right) & \text{for } a > 0 \text{ and } b < 0 \end{cases} \tag{2}$$

The Hue attributed to the color whereby recognized as being predominantly red, green, blue, yellow, violet, etc. The hue angle reported as a degree in range of 0° (red), 90° (yellow), 180° (green), and 240° (blue) and back to 0°.

The color fastness of dyed wool samples to wash and the light assessed according to ISO standard test method. Color fastness against wash carried out according to ISO105-CO2:1989, and color fastness against light assessed according to ISO105-B02:1994.

3 Results and Discussion

3.1 UV–Vis Spectroscopy Results

The optical absorption spectrum is a crucial technique for characterization of metal nanoparticle structures. A decrease in the size of noble metals in the bellows electron free path results in intense absorption invisible-near-UV [22]. Therefore, the optical absorption spectrum is a crucial technique for the characterization of metal nanoparticles structure. The UV–Vis absorption spectrum of indigo-dyed wool samples (Fig. 1) showed a maximum absorption peak around 610 nm, which is the characteristic peak of indigo and reported by other researchers [23]. The presence of the absorption peak near 410 nm for the silver treated indigo-dyed wool fabric samples confirmed the synthesis of spherical shaped AgNPs [15] during the indigo dyeing process. If only one single symmetric extinction peak appears around 400 nm, it confirms that the spherical shape of silver nanoparticles is formed [15]. The characteristic peak of spherical AgNPs usually occurs around 400 nm, which means did not fully bond with the indigo molecular colorant. Moreover, the extract solution of pristine wool fabric did not present any peak around this position (Fig. 1).

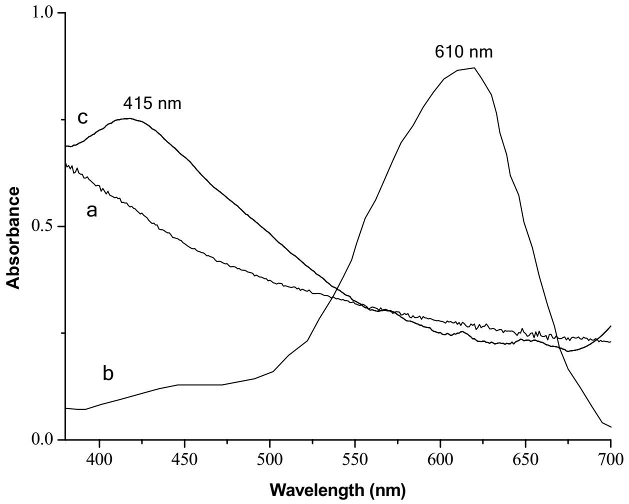


Fig. 1 The UV–Vis absorption spectrum of the extracted solution of (a) pristine wool sample, (b) indigo-dyed wool sample, and (c) silver treated indigo-dyed wool sample

3.2 Surface Morphology and Elemental Analysis Results

The scanning electron microscope used for observing the surface morphology of wool fibers. The SEM images of pristine wool fibers and indigo-dyed samples presented (Fig. 2) a cuticle scales structure at the outer layer of the wool surface (Fig. 2a), which is the directional overlapped structure. The scale surface morphology of the treated wool samples were altered compares to the pristine sample, and the surface of treated samples converted to the rough surface due to the presence of small platelets of crystal indigo structure (Fig. 2b, c). The SEM images of indigo-dyed wool fiber samples indicated the formation of indigo crystal with micro-size platelet-like structure, which partially dispersed on the surface of the wool fiber. Indigo crystal grows almost with a macroscopic platelet-like structure and this structure owes to the formation of the layered packing in its crystal structure, which held by the strong inter-molecular hydrogen bonds. The edges of the platelets rapidly grow at

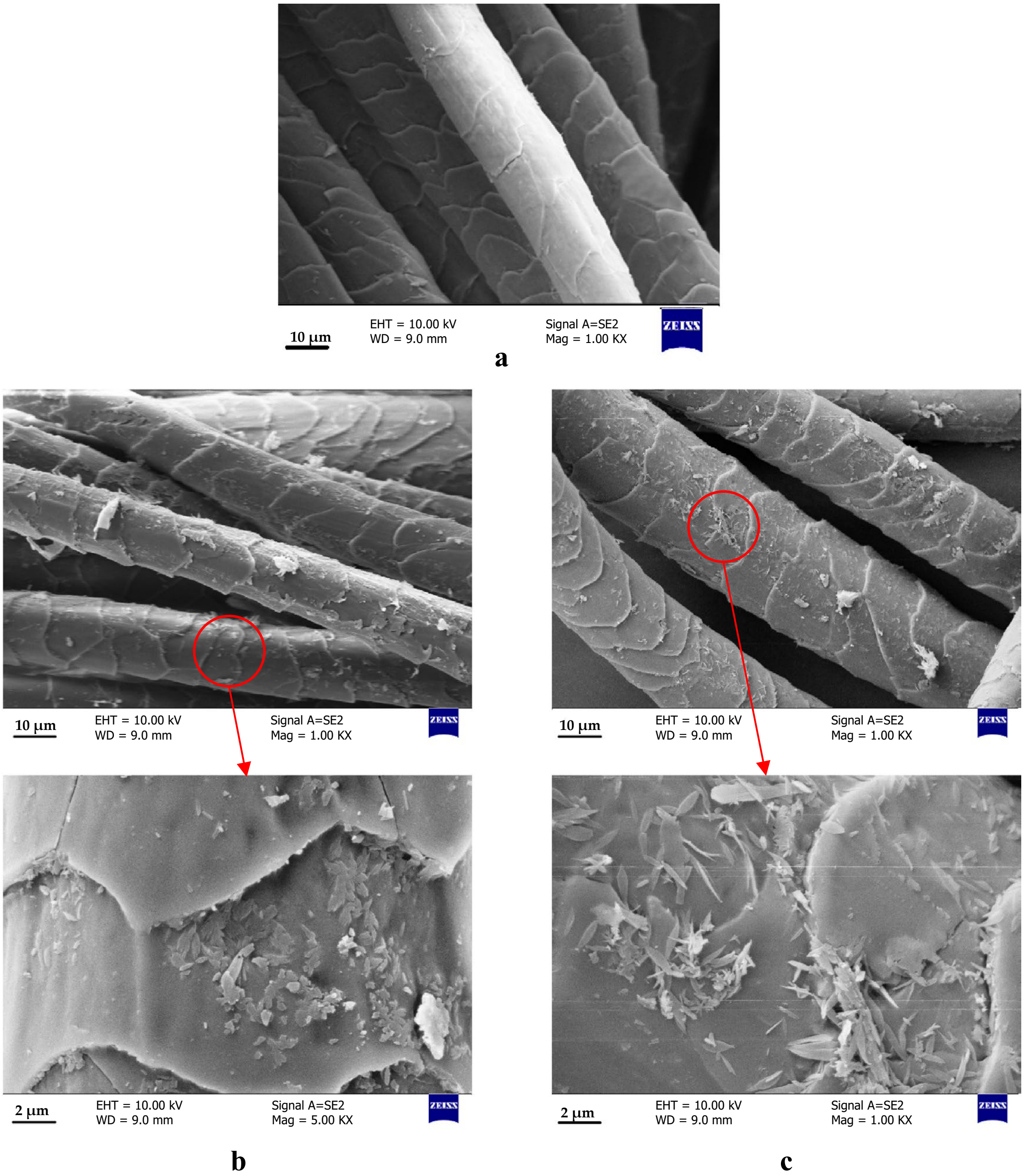


Fig. 2 The SEM images of wool fiber surface which are **a** pristine fiber sample, **b** silver pre-treated indigo-dyed wool sample and **c** simultaneous silver treated indigo-dyed wool sample during the dyeing process

crystallisation process and therefore the "active" surface area will be dominated by these edge areas rather than the plane area. The platelet structure at molecular level is reflected in the formation of thin crystal plates at macroscopic level [18].

Indigo colorant is highly water-insoluble due to strong hydrogen-bonding interactions in the layered solid-state structure. Therefore, before the dyeing process, it is necessary to reduce the water-insoluble form of the indigo colorant into the water-soluble *leuco*-form. The indigo molecular structure presents a platelet-like structure which is held by the strong intermolecular hydrogen bonds [18]. During the reduction process of indigo colorant (*leuco*-indigo formation), both the interactions between and within platelet need to overcome. On the other hand, under adequately alkaline conditions, the presence of metal cations will lead to slow delamination and the disintegration of the indigo platelet. Hence, the presence of silver cation or silver nanoparticle has enhanced the dissolution process and resulted in better dyeing properties. Finally, the absorbed *leuco*-form of indigo should oxidize to the water-insoluble structure and resulted in a formation of thin crystal platelets at the macroscopic level. The platelets size distribution histograms of indigo are presented in Fig. 3. The silver pre-treatment resulted in a formation of smaller indigo platelets (0.73 µm) compare to the silver simultaneous treatment method (1.46 µm). It believes that the presence of silver nanoparticle provided nuclei on the wool fiber structure for the formation of indigo particles [24] and resulted in the small platelet-like particles. The hydroxide concentration can affect the size of indigo platelet-like. The higher concentration result to formation a smaller indigo platelet-like during crystallization process. A higher alkalinity may be better for preventing aggregation effects and for generally improving *leuco*-indigo solubility and diffusivity [25]. In addition, it has been reported that the presence of cation results in a significant sedimentation of the indigo and formation of larger indigo platelet-like [24]. Therefore, the presence of silver ions at the silver simultaneous treatment method may led to lower pH and reduce the solubility of *leuco*-indigo, which was resulted in a larger indigo platelet-like.

The elemental analysis of indigo-dyed wool fabric samples is presented in Fig. 4. The EDS spectra confirm the presence of AgNPs on the surface of indigo-dyed wool fibers. In addition, the presence of other elements such as carbon, oxygen, sulfur, and nitrogen on indigo-dyed wool fibers related to the indigo colorant and wool fiber components. Moreover, the presence of gold element on the surface of indigo-dyed wool fibers is due to gold sputtering of samples before capturing images.

3.3 Silver Nanoparticles Formation Mechanism

Wool fiber has polar and ionizable groups which bind to opposite charged organic or inorganic molecules [26]. Carboxyl group (–COOH) on the amino acids, carbonyl group (C=O) on the indigo molecular structure and hydroxyl group (OH) on the water-soluble *leuco*-form of the indigo molecular structure are the most important binding sites that provide interaction with silver cation. During the dyeing process, silver cation (Ag^+) absorbed by the above functional groups due to electrostatic interaction. The Ag^+ reduced to a silver atom (Ag) during the reduction process of indigo colorant (*leuco*-indigo formation) with sodium dithionite. Sodium dithionite is an inexpensive reducing

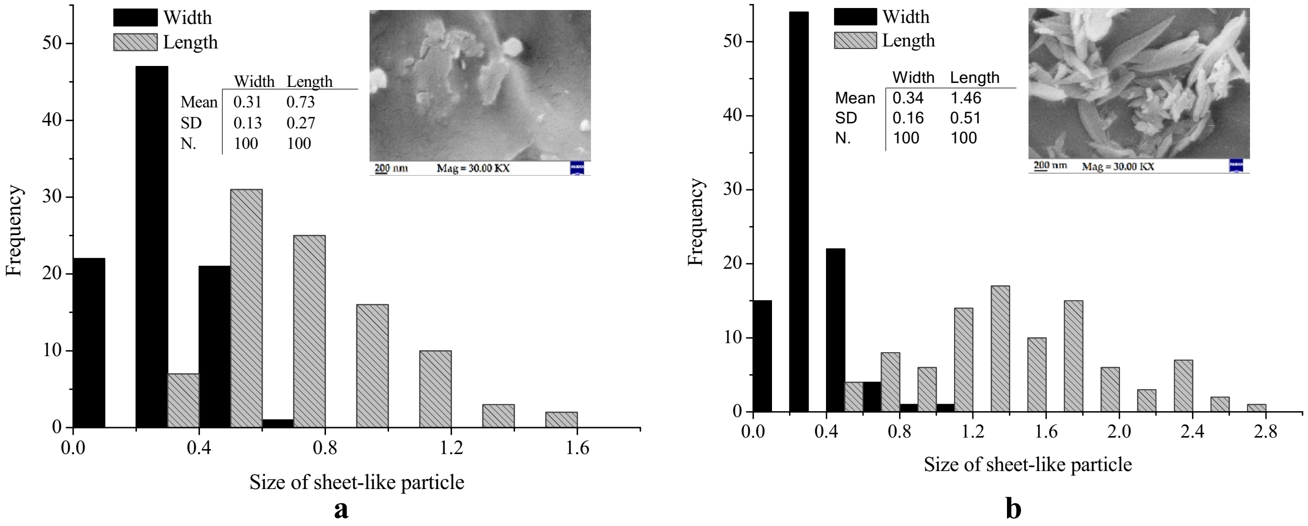


Fig. 3 The size distribution histograms of platelet-like particles of indigo colorant for **a** silver pre-treated indigo-dyed wool sample and **b** simultaneous silver treated indigo-dyed wool sample during the dyeing process

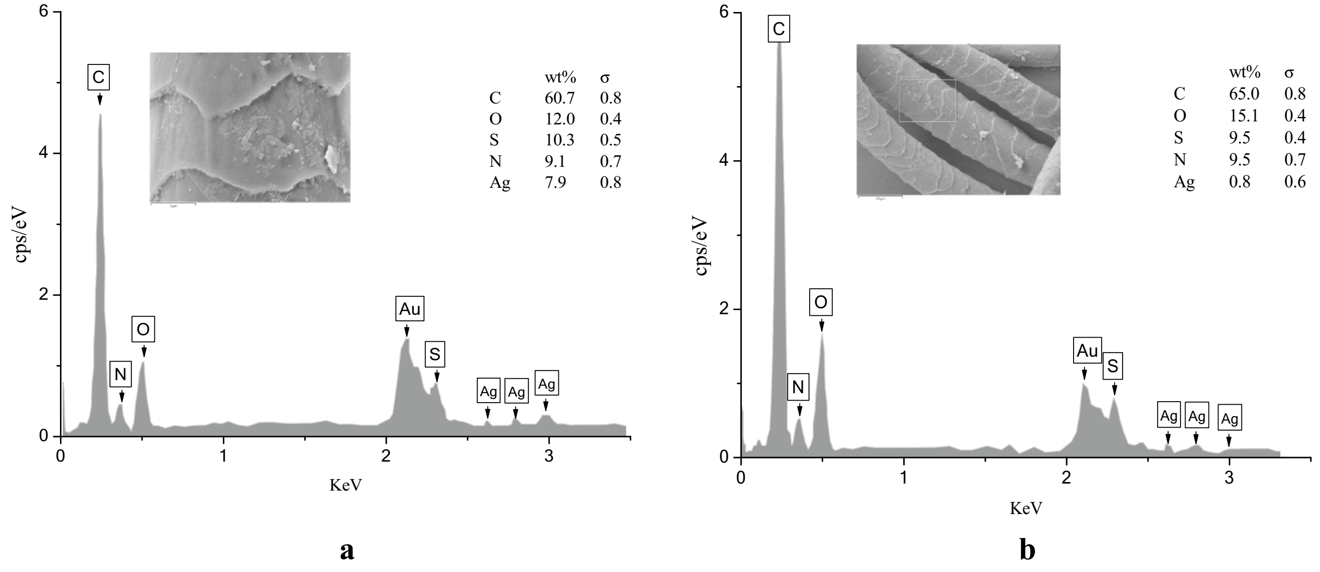


Fig. 4 The EDS spectrum of wool fiber samples which are **a** silver pre-treated indigo-dyed wool sample and **b** simultaneous silver treated indigo-dyed wool sample during the dyeing process. The insert SEM images indicated the area selected for EDS analysis

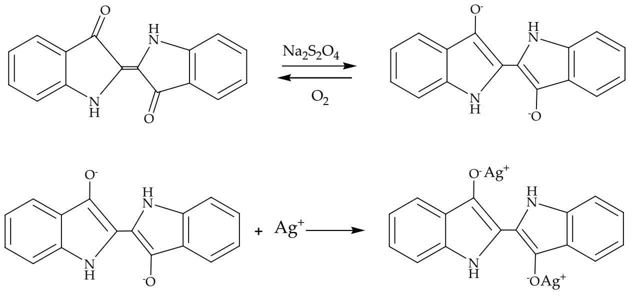


Fig. 5 Proposed interaction mechanism of silver with water-soluble *leuco*-form of indigo molecular

agent since 1 mol dithionite can precipitate 2 mol of silver in the reaction system and process efficiency of silver reduction has been higher than 99% in 45 min [27]. Therefore, the absorbed silver ions reduced at the proposed dyeing procedure for 50 min. The synthesis of AgNPs in the presence of sodium dithionite solution performed according to the following equation at alkali condition:

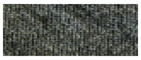
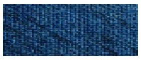
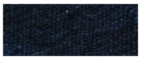
$$S_2O^{2-}_{4(aq)} + 4OH^{-}_{(aq)} + 2Ag^{+}_{(aq)} \Rightarrow 2Ag^{0}_{(s)} + 2SO^{2-}_{3(aq)} + 2H_2O \tag{3}$$

Sodium dithionite reduced the silver ions in the indigo-dyeing solution (Fig. 5) or bonded to the wool fiber structure in the pre-treatment process. The primary AgNPs coalesced with each other and formed large nanoparticles that also known as secondary nanoparticles. The silver atom clustered and created nanoparticles. Synthesis of AgNPs resulted in the brown-yellowish color of the wool fabric samples that did not dye with an indigo colorant (SIAg0, and PAgI0).

3.4 Colorimetric Characteristics of Dyed Wool Samples

The colorimetric data of indigo-dyed wool samples are presented in Table 2. The Hue attributed to color whereby recognized as being predominantly red, green, blue, yellow, and violet, etc. The Hue angle is reported as a degree that is ranging from 0° (red) through 90° (yellow), 180° (green), and 270° (blue) and back to 0°. The indigo-dyed wool samples without any silver treatment presented a hue angle between 255° and 271°, which confirmed a blue shade on the dyed wool fabric (sample code; Indigo1, Indigo3, and Indigo6). Moreover, the silver treated undyed-wool samples showed a hue angle between 70° and 94° and had a pale yellow and brown-yellowish shade which confirmed the formation of AgNPs on their surface (sample code; SIAg0 and PAgI0) (Table 2). The position of indigo-dyed wool samples in the CIELAB color space is presented in Fig. 6. The yellow and brown samples located in zone A, and blue samples stayed in zone C. The chromaticity and lightness of untreated-indigo dyed wool samples and silver treated indigo-dyed wool samples are presented in Fig. 7. As it can be seen, silver pre-treated indigo-dyed samples had the lowest chromaticity and lightness located in zone B. Synthesis of AgNPs on wool fibers surface resulted in the low chromaticity values (PAgI0) with brown-yellowish shade and would result in dull shades. Therefore, pre-treated wool sample with silver ions, then dyeing with indigo colorant resulted in a dark blue

Table 2 The colorimetric data (L*, a*, b*, C* and h*) for indigo-dyed wool samples with and without silver treatment (Color Table online)

ID	L*	Hue	Chroma	Relative color strength	Sample
Un-treated	80.64	87	15.4	100	
SIAg0	74.72	94	10.3	137	
SIAg1	58.76	144	6.1	376	
SIAg3	38.34	245	15.1	1284	
SIAg6	27.24	263	16.5	2517	
PAgI0	48.29	70	11.4	743	
PAgI1	26.04	214	3.5	2892	
PAgI3	20.58	228	1.8	4216	
PAgI6	15.85	323	1.7	5573	
Indigo1	37.14	255	21.2	1440	
Indigo3	29.67	261	20.2	2274	
Indigo6	22.06	271	16.5	4121	

shade (Hue Angle$_{PAgI1}$ = 214, Hue Angle$_{PAgI3}$ = 228) and low brightness. However, simultaneous silver treatment method (SIAg3 and SIAg6) resulted in blue shad and higher chromaticity values compared to the silver pre-treatment method.

The color strength (K/S) spectra of untreated-indigo dyed wool samples and silver treated indigo-dyed wool samples are given in Fig. 8. Compared to silver treated indigo-dyed wool fabrics, the untreated indigo-dyed wool samples presented lower color strength at all visible wavelengths. Among the undyed samples, the silver pre-treated sample (PAgI0) had the highest color strength due to higher loading AgNPs. The silver pre-treated indigo-dyed samples presented a higher relative color strength compare to the simultaneous silver treated indigo-dyed samples at each concentration. The presence of AgNPs on the surface of wool fiber can enhance the adsorption of indigo molecule and resulted in higher dye uptake as well as relative color strength [28]. The simultaneous silver treated wool sample presented a lower color strength compare to silver pre-treated sample, due to lower AgNPs content. The simultaneous silver treatment method resulted in the synthesis of an un-stable colloidal solution that easily agglomerates on the wool fabric, and could not diffuse into the wool fiber structure. Thus, the synthesized AgNPs deposited only on the fiber surface that can easily remove at the washing process. Therefore, the low AgNPs content resulted in a pale yellow color with a low color strength.

The simultaneous silver treated indigo-dyed wool sample had a blue color shad with a lower color strength compared to untreated indigo-dyed samples. The interaction between the water-soluble *leuco*-form of indigo molecular and silver followed in the treated solution and the outer structure of wool fiber that resulted in the lower exhaustion according to

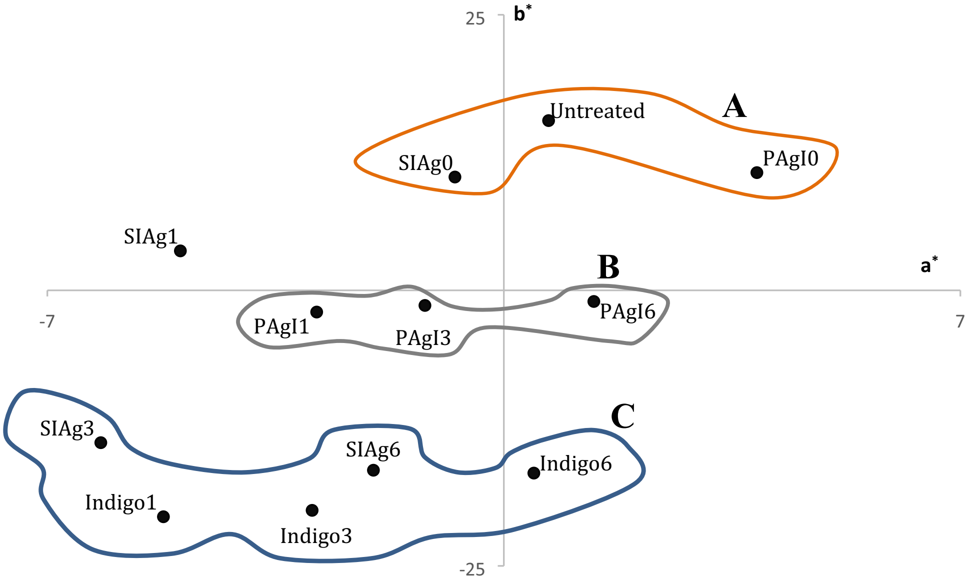


Fig. 6 The position of indigo-dyed wool samples at CIELAB color space. The yellow and brown samples located at zone A, while silver pre-treated indigo-dyed wool samples had the lowest chromaticity and lightness located at zone B and blue dyed samples stayed at zone C (Color figure online)

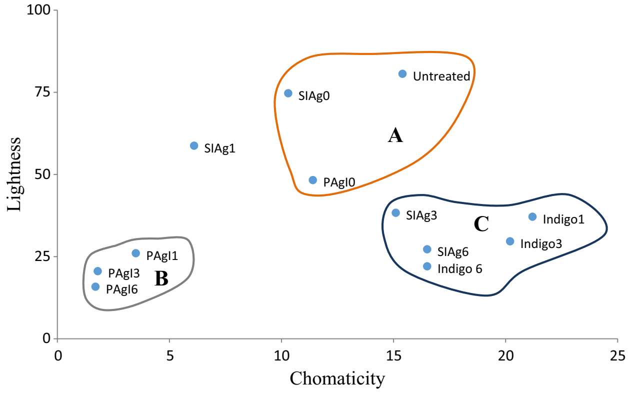


Fig. 7 The chromaticity and lightness of un-treated and silver treated indigo-dyed wool samples. The yellow and brown samples located at zone A, while silver pre-treated indigo-dyed wool samples had the lowest chromaticity and lightness located at zone B and blue dyed samples stayed on zone C (Color figure online)

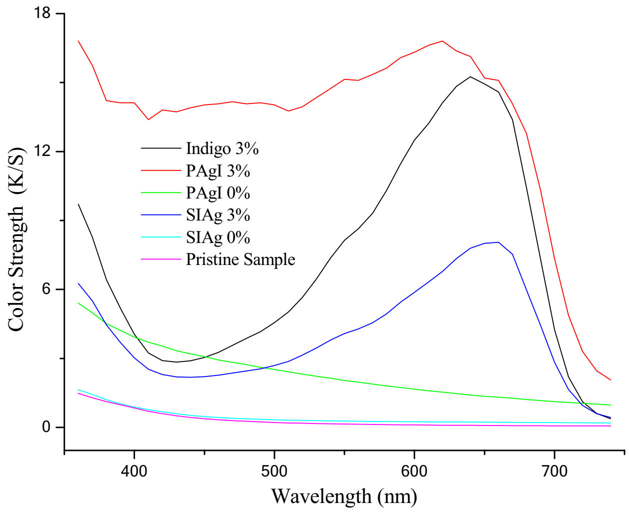


Fig. 8 The color strength (K/S) spectra of un-treated and silver treated indigo-dyed wool samples (Color figure online)

the lower color strength. While, in the case of the silver pre-treated indigo-dyed wool samples, the interaction of silver and water-soluble *leuco*-form of indigo followed inside of the wool fiber structure. As a result, these samples showed a dark blue color shad with a higher color strength compared to untreated-indigo dyed samples.

In addition, the results indicated that the silver pre-treatment method led to higher indigo uptake. In order to enhance the indigo uptake during the dyeing procedure, a metal salt pre-treatment has been suggested [29, 30]. Effect of different metal salts on color strength has been investigated in various researches [29, 31–33]. These studies have shown that only the metal salts like Ag, whose metal hydroxides are insoluble in water and converted to their higher oxidation state are effective in increasing the color strength. Moreover, the silver cation is a weak acid and hence, its hydroxide precipitates at relatively high pH. Therefore, the silver pre-treated indigo-dyed woollen yarn had higher indigo uptake.

Lightness (L^*) is one of the color appearance parameters of any dyed model and considerably depends on the surface luster and specular reflectance of the dyed sample. The silver pre-treated indigo-dyed wool sample had a low lightness value, which can be due to the lower specular reflectance. The metallic salt as a mordant has a significant effect on the shade lightness of dyed fabric with natural colorants [34]. On the contrary, the simultaneous silver treated indigo-dyed wool sample showed higher lightness compared to the dyed sample with the same indigo concentration. In this case, simultaneous synthesis of AgNPs in the dyeing bath resulted in the lower exhaustion and color strength.

3.5 Fastness Properties of Dyed Samples

The wash and light colorfastness of indigo-dyed wool yarns are presented in Table 3. In order to find out the fastness properties, the indigo-dyed samples with the same concentration of indigo colorant compared. The wash and light fastness assessed based on the grayscale and blue scale accordingly. In general, among other classes of dyes, indigo-dyed fabrics showed higher wash fastness properties. An insoluble characteristic of the indigo colorant is the reason for this superior wash fastness. Therefore, all indigo-dyed woollen yarn samples presented an excellent washing fastness [29, 31–33].

The experimental results indicated that all indigo-dyed woolen yarns presented an excellent light fastness property. Indigo colorant has a good light fastness property, which is independent of substituent groups. This factor, combined with the physical state of the dye, may explain its superior lightfastness compared to other natural dyes [35].

4 Conclusion

AgNPs synthesized through two different methods such as pre-treatment and simultaneous silver treatment during indigo dyeing procedures. Sodium dithionite used to reduce the water-insoluble indigo, as well as for synthesizing

Table 3 Fastness evaluation of indigo-dyed wool fabric

Sample	Light fastness	Wash fastness	Staining on cotton	Staining on wool
Indigo3	6–7	4–5	5	5
SIAg3	7–8	4–5	5	5
PAgI3	7–8	4–5	5	5

AgNPs. A decrease in the size of noble metal particles to the bellow electron free path gives rise to intense absorption in the visible-near-UV. Maximum absorption wavelength of the indigo colorant appeared around 610 nm. Moreover, there was an absorption peak near to 410 nm, which was due to the presence of AgNPs on the indigo-dyed wool fabrics and confirmed the synthesis of spherical AgNPs. The SEM images of indigo-dyed wool fiber samples indicated the formation of indigo crystals with micro-size platelet-like structures, which partially dispersed on the surface of the wool fiber. The silver pre-treatment method resulted in the formation of smaller platelets particle of indigo colorant compare with simultaneous silver treatment method. It believe that the presence of AgNPs provided nuclei on the wool fiber for the formation of indigo particles and resulted in the smaller platelets particle. The indigo dyed wool samples, without any silver treatment, presented with a hue angle between 255° and 271° due to the appearance of a blue shade. While the silver treated undyed-wool samples showed a hue angle between 70° and 94°, which was due to the appearance of the pale brown-yellowish shade of AgNPs on their surface. The indigo-dyed wool sample without any silver treatment resulted in a lower color strength at all visible wavelengths. Moreover, the silver pre-treatment method resulted in higher color strength due to its higher AgNPs content compared to the simultaneous silver treatment method.

The simultaneous silver treatment method resulted in the synthesis of an un-stable colloidal solution that easily agglomerates on the wool fabric, and could not diffuse into the wool fiber structure. While, in the case of silver pre-treatment method, the interaction of silver and water-soluble *leuco*-form of the indigo colorant followed inside of the wool fiber structure. As a result, these samples showed a dark blue shade with higher color strength compared to untreated-indigo dyed samples.

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