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Silver Nanoparticles Synthesized on the Wool Yarns with Safflower Natural Dye: Colorimetric and Fastness Studies

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ABSTRACT

The research and development of green techniques for the synthesis of silver nanoparticles (AgNPs) with bioactive plants has gained more attention against toxic chemicals. In this research, the aqueous solution of safflower extract was utilized for the simple, green, and commercial synthesis of AgNPs from $AgNO_3$ solution on the wool yarn. The effect of the amount of extract and $AgNO_3$ on the properties of produced nanoparticles was studied. The analysis of AgNPs by Dynamic Light Scattering (DLS) system and Ultraviolet-visible (UV-Vis) spectroscopy exhibited that the particle size of produced NPs was <57 nm. In addition, the colorimetric data of wool yarn dyed with safflower extract in the presence of different concentrations of $AgNO_3$ solution were also studied. The results showed that the presence of nanoparticles changed the color hue (h^o: 86→58), and the absorption of safflower extract on the wool samples increased from 5 to 29. Also, the ratings of washing and rubbing fastness of dyed samples were satisfactory (4-5). Prog. Color Colorants Coat. 17 (2024), 325-332© Institute for Color Science and Technology.

1. Introduction

Wool is an ancient protein fiber and thanks to its special structures such as unique flexibility, moisture absorption and resistance to wrinkles, it has various applications [1-3]. Despite the mentioned advantages, they are a suitable environment for the formation and transmission of microorganisms at appropriate humidity and temperature. The colonization of microorganisms in wool fibers can lead to skin irritation, destruction, bad odor and color change of products. Therefore, wool products with good quality must prevent the growth of microorganisms and also the damage caused by them on the fibers [4-6].

Several chemicals are used to provide the antibacterial activities on the natural textiles. Most of them pollute the environment and can be dangerous and toxic for consumers of products. Until now, various nanoparticles have been used for antibacterial finishing of textiles. Among the metal nanoparticles, silver nanoparticles (AgNPs) have been utilized in many productions because of their exceptional biological, chemical, catalytic, electronic and optical properties [7-9]. The research and development of green techniques for synthesis of silver nanoparticles with natural compounds has attracted more attention, in which instead of toxic chemicals are utilized. Most of the offered systems are based on the green chemistry with a special focus on the use of natural compounds extracted from plant origin [10-12]. By the way, the green synthesis of silver nanoparticles using

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agricultural and industrial waste or food as a regenerating and stabilizing source can be a valuable method. Until now, different parts of plants and their waste have been used for the synthesis of different nanoparticles such as rice husk extract, henna leaf, green tea, *Camellia sinensis*, and so on [13-15].

Currently, the colorants extracted from natural origins are becoming increasingly popular as a substitute for synthetic dyes in textile dyeing and finishing processes [3-7]. Recent reports shows the potential for a wide-scale dyeing of textile by natural dyes due to their high economic value and waste management [8, 9]. As examples of recently published work explored yellow dyes with high stability, antioxidant, and antibacterial properties from the waste leaves of *G. biloba*, *E. japonica*, *C. camphora*, *S. sebiferum*, *F. artemisiae argyi*, and waste peanut skins aqueous extract for dyeing wool fibers with metal salts and bio-mordants [8-11].

Safflower (*Carthamus tinctorius*) is an ancient plant that were used in medicinal and food area [16, 17]. This crop contain large amounts of linoleic acid, vitamins A and E, unsaturated fatty acids, and other bioactive ingredients due to their antioxidant, antiseptic and antibacterial properties. The isolated compounds from the safflower plant contain polysaccharides, quinochalcones, polyacetylenes, flavonoids, fatty acids, , alkaloids steroids, lignans and proteins. It has suggested that quinochalcones and flavonoids are the main bio-active ingredients can alter metal ions into nanoparticles [18, 19]. The simplicity of the synthesis, lack of toxic compounds, and easy operating conditions are several advantages of the synthesis of metal nanoparticles using plant extracts other than chemical and physical methods [20-22]. In addition, the exceptional biological activities even more than their commercial materials was observed by silver nanoparticles synthesized by the green methods [15, 16]. The safflower plant can be proper for the production of Ag nanoparticles due to the presence of phenolic compounds and other ingresients with the ability to reduce metals. However, the application of safflower plant for the synthesis of nanoparticles has been paid little attention. It was reported that the extract of safflower plant in the ethanol can be easily produced silver nanoparticles by antibacterial activity with an average size of about 20 nm at room temperature [23, 24].

Although there are a limited number of reports about the use of safflower extract as a reducing agent green for synthesis of silver nanoparticles, the object of the current study is the synthesized nanoparticles with safflower extract in dyeing process of woolen yarns. For this purpose, wool fabric were dyed by different concentrations of safflower extract and silver nitrate solution. UV-Visible and DLS analyses were used to determine the size of silver nanoparticles. Also, the dyeing and fastness properties of the wool samples were evaluated.

2. Experimental

2.1. Materials

The laboratory-grade of silver nitrate was purchased from Merck, Germany. The safflower plant was prepared from the medicinal plants of the Taj Mahal. The flower part was completely dried in shade, crushed, and milled to get a fine powder. This fine powder was used for dye extraction and dyeing trials without any further purification. The specification of white woolen yarn was 200 tex 4 folds used to develop hand-made carpets were chosen for this study and it was obtained from Azar Baft company. The distilled water was used as a solvent and the rest of solvents and chemicals were of laboratory grade.

2.2. Equipment

The UV-Vis spectrum of the solution was measured by the cecil 9200 double beam UV-Vis spectrophotometer, England, after diluting the sample. The average size of silver nanoparticles was measured by dynamic light scattering (HORIBA, Japan). The amount of color absorption of the dyed product was measured by the Color-Eye 7000A device manufactured by Gretag Macbeth, USA.

2.3. Extraction of safflower and biosynthesis of silver nanoparticles on wool yarn

5 g of the ground powder of the flower part of the safflower plant was placed in distilled water (100 mL) and heated at boiling temperature for 2 hours. Then, the soluble part was separated through filter paper. The resulting solution was stored at 4 ºC to be used as the mother extract in the next experiments. Also, 10 mM silver nitrate was prepared and used as silver mother solution in the experiments. Different ratios of extract and silver solution were prepared, mixed with each other and used for dyeing woolen yarn (Figure 1).

Figure 1: Scheme of Ag NPs synthesized on the wool by safflower extract.

Before dyeing, the wool fabric was washed in a solution containing non-ionic detergent and ammonium hydroxide (pH=8-9) for 20 minutes at 70 °C. Next, the woolen fabrics were dyed according to the graph given in Figure 2.

After dyeing, the washing of dyed samples was performed by warm and cold water, respectively. To measure the colorimetric data of wool yarns, the reflectance of them was measured by a reflectance spectrophotometer at the wavelength of 400 to 700 nm, and then the color strength (K/S) was computed according to Eq. 1. In this equation, R represents the reflection of the sample at each wavelength.

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

To perform the washing fastness test, first a composite sample was prepared, which includes adjacent wool, cotton and dyed sample, then the national standard of Iran 10076 ISIRI was used according to the instructions given in Table 1. After the composite samples were washed, the color change of dyed samples and staining ratings on the adjacent fabrics were evaluated based on the gray standard. Also, ISIRI 205 standard was used to perform light fastness test. The color change caused was evaluated by the blue scale.

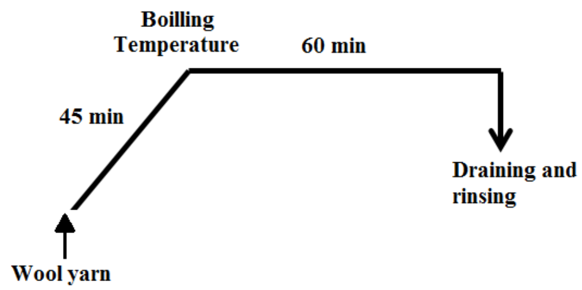

Figure 2: Dyeing method of wool yarn (Acetic Acid 1 %, pH= 4-5 and L.R:40.1)

Table 1: Instructions for washing fastness (national standard of Iran 10076 ISIRI).

Time (min)	Detergent (g/L)	Temperature (°C)	L:R
30	5	40±2	50:1

3. Results and Discussion

3.1. UV-Visible spectroscopy

UV-Visible spectroscopy is used as an important technique for analysis of nanoparticles in the solution, and it is a confirmed method to verify the produced Ag nanoparticles in the extract solution [20, 21]. The interaction between the different ratios of safflower extract and the silver solution was measured by an UV-Visible spectrophotometer (Figure 3). Due to the motivation of surface plasmon vibrations in silver nanoparticles, the shift of the color solution from yellow to brown is occurred. The successful synthesis of silver nanoparticles is evident by absorption peak in the range of 480-500 nm. Results indicated that there is no a clear peak above the 480 nm range for the absorption spectrum of the extract. The new peak at 480-500 nm was appeared when the reaction of the extract with silver ions was performed, and consequently AgNPs was produced (Figure 1). This result is basically consistent with the visual observation of color and shows that safflower extract is able to reduce Ag^+ to Ag^0. The obtained results are consistent with the previous study reported by the researchers, which shows that silver nanoparticles can be produced using safflower [20, 21].

The increasing of absorbance in the range of 480 nm indicates the rapid reduction process of silver ions to AgNPs, and consequently the more silver nanoparticles is formed (Figure 1). The wavelength of the maximum plasmonic absorption of silver nanoparticles is affected by the nanoparticles size, and by increasing in the size of the particles, the width of the wavelength increases. The results showed that the size of produced AgNPs is small. Otherwise, according to the Mie theory, spherical nanoparticles can be produced only by one SPR band, while two or more SPR bands are estimated to form according to the shape of the particles in the absorption spectrum of anisotropic fragments [23].

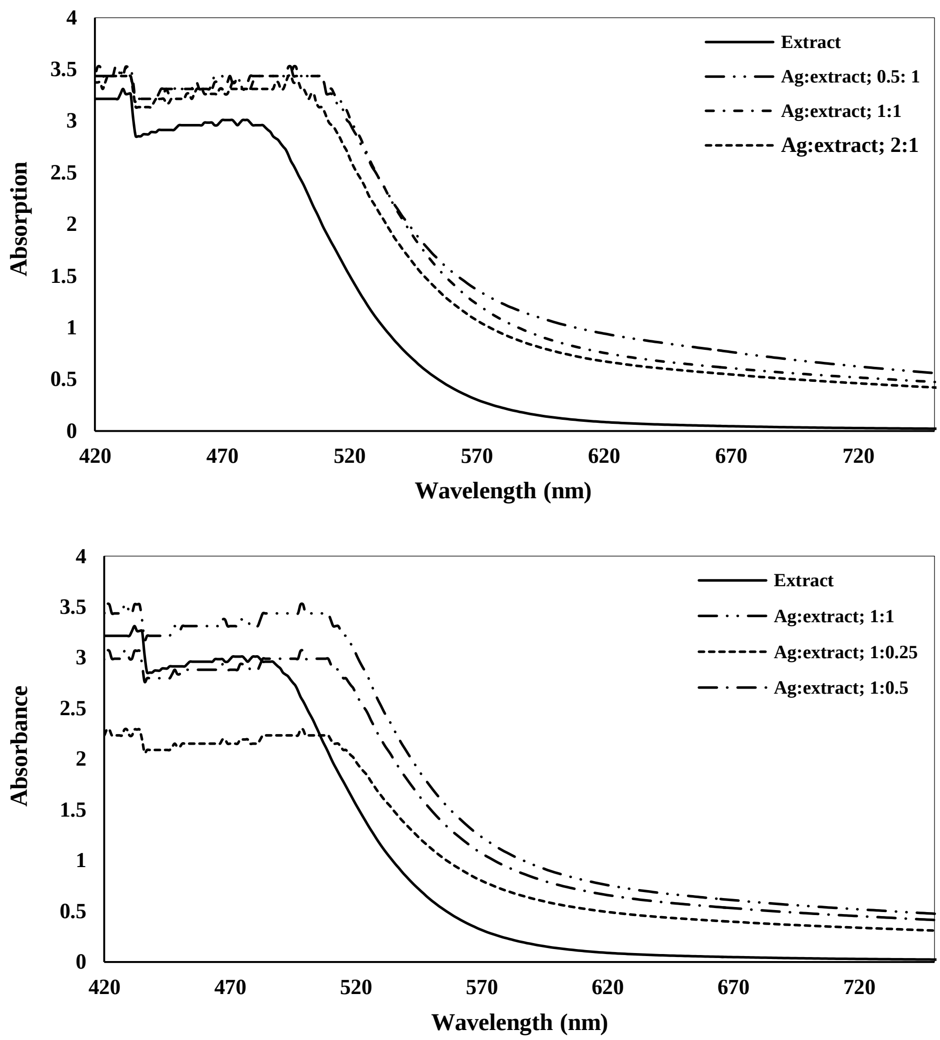

Figure 3: UV-Visible spectra of Ag nanoparticle at different ratios.

Reports indicate that the reduction of metal ions to nanoparticles is performed by natural active ingredients are available in the extract, and the formed nanoparticles include as capping agents. It was found that only a weak band with an absorption maximum wavelength was observed at λ_{max} = 480 nm in the low ratios of extract (0.25:1 and 0.5:1). By gradually increasing the amount of extract to 1:1, the absorption intensity of silver nanoparticles at about 480 nm considerably increased and arrived a maximum. Obviously, the number of produced AgNPs increased by the increasing amount of extract, and the obtained results are as per reported by the researchers. However, since safflower extract is very concentrated, extracts with higher concentrations cannot be measured. Moreover, the absorption spectrum of the extract and $AgNO_3$ mixtures in diverse ratios also shows a band with a low shift, which indicates the different sizes of AgNPs. With increasing of silver amounts, the absorption with the extract increased steadily and reached the maximum at ratio of 1:1. There was no observable variation in absorption with increasing of $AgNO_3$ ration (1:2). Results indicated the biosynthesis of AgNPs with a 1:1 ratio of 10 mM $AgNO_3$ and safflower extract (1 %) shows the maximum absorption, and the reducing of Ag ions by safflower extract is completed.

3.2. Determination of the size of synthesized AgNPs

The size of AgNPs is considered as an important factor, so that the amount of extract considerably affects the particle size, but it has a insignificant influence on the shape of nanoparticles [24, 25]. After determining the best conditions for the synthesis of nanoparticles using UV-Vis, the ratio of extract and $AgNO_3$ 1:1 was prepared, and the average size of silver nanoparticles was determined by DLS. DLS is an analytical method that estimates the particle diameter along with the external phytochemical coating, which is usually called the hydrodynamic diameter. The average size of biosynthesized silver nanoparticles is shown in Figure 4. The results showed that the optimal concentration of the extract is necessary for the reduction and stabilization of nanoparticles. If the concentration is outside this limit, the nanoparticles are obtained in smaller amounts and with larger sizes or they accumulate, which causes the particles to become larger. With the increase of the extract concentration, the average size of silver nanoparticles biosynthesized by the extract gradually decreased and when the ratio was 1:0.5, it reached a minimum and dramatically decreased to 28 nm (Table 2).

Table 2: DLS data of Ag nanoparticle at different ratios.

Sample	Particle size (nm)
Extract and $AgNO_3$ 1:0.5	28
Extract and $AgNO_3$ 1:1	57
Extract and $AgNO_3$ 1:2	382
Extract and $AgNO_3$ 0.5:1	514
Extract and $AgNO_3$ 0.25:1	750

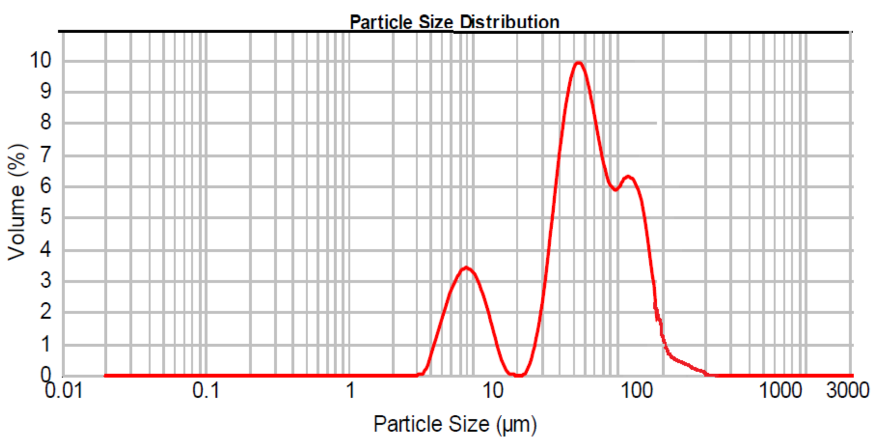

Figure 4: DLS data of Ag nanoparticle at different ratios.

3.3. Dyeing characteristics of dyed wool yarn

The effect of the amount of Ag on the safflower extract absorption on the wool yarnis given in Table 3. Results indicated that the color strength of dyed samples with safflower extract increased from 5.92 to 29.45 in the presence of Ag NPs. Therefore, silver nanoparticles can act as a metal mordant to bind dye on wool. The absorption of safflower extract on the wool yarn was lower than all samples dyed with silver ion [25]. Samples dyed with safflower extract and Ag ions produced more functional groups than wool yarn. Ag ions can regenerate safflower extract and can also be adsorbed on wool yarn. Therefore, there are more reactive sites on the wool yarn that can bind to the dye molecules and also improve the absorption of safflower extract. The size, shape and dielectric properties of AgNPs can change the colors from yellow to red or blue. It seems that the AgNPs loaded on the fabric form a yellow-brown color that enhances the absorption of safflower extract. the reflectance values of the dyed samples with Ag ions decreased significantly, which could be due to the appearance of yellowish brown color on the dyed samples due to the synthesis of silver nanoparticles [26].

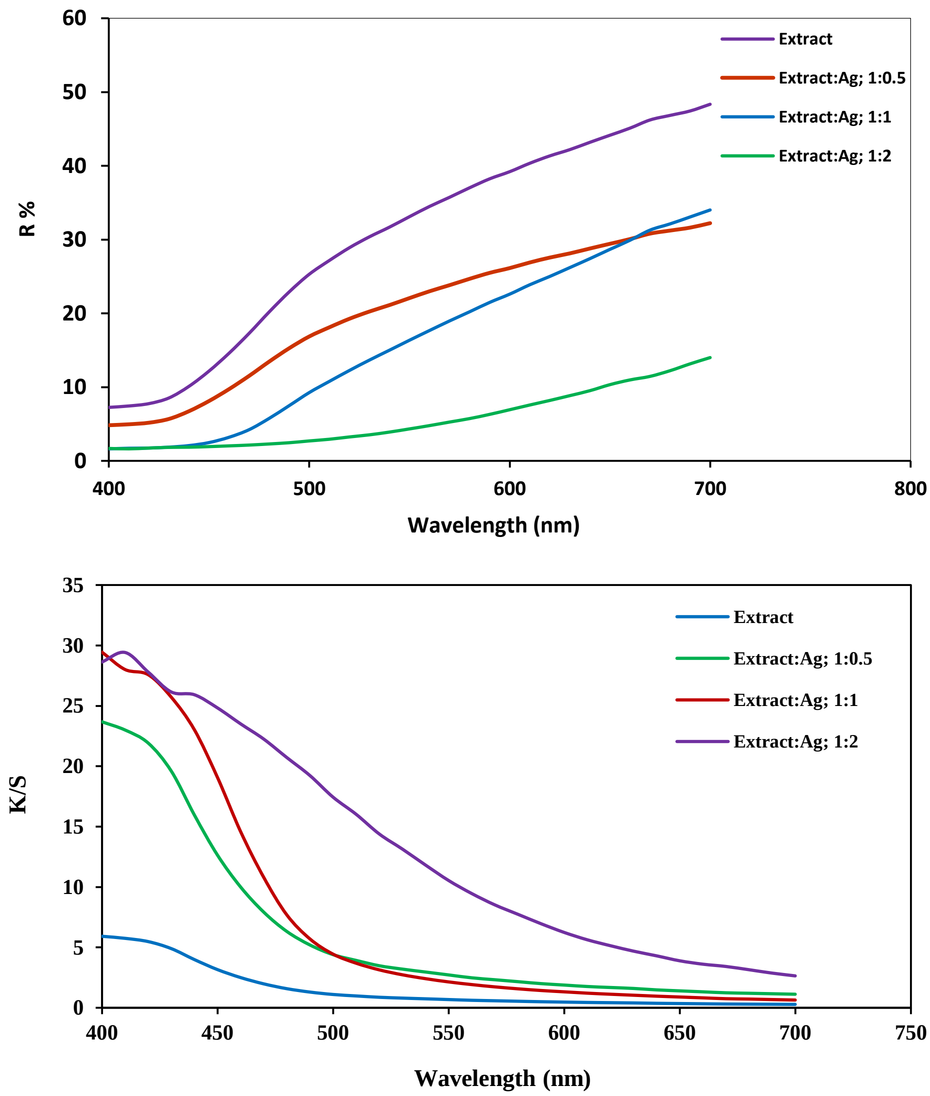

Figure 5: Reflectance and color strength curves of wool samples dyed with different ratios of extract and Ag.

Table 3: Colorimetric data of wool samples dyed with different ratios of extract and Ag.

Sample	L*	a*	b*	C*	h	K/S
Extract	63.71	2.14	34.82	34.88	86.48	5.92
Extract:Ag; 1:0.5	49.64	6.75	40.86	41.41	80.61	23.58
Extract:Ag; 1:1	47.29	8.98	44.75	45.64	78.66	29.45
Extract:Ag; 1:2	26.03	11.01	18.03	21.12	58.59	28.63

Table 4: Colorfastness characteristics of wool samples dyed with different ratios of extract and Ag.

Sample	Rubbing fastness		Washing fastness			Light fastness
	Wet	Dry	Ch	W^s	C^s	
Extract	3-4	4	3-4	4	4-5	3-4
Extract: Ag; 1:0.5	4-5	4-5	4	4	4	4
Extract: Ag; 1:1	4-5	4-5	4-5	4	4-5	4
Extract: Ag; 1:2	5	5	5	5	5	4

Ch: color change, Cs: staining on cotton, Ws: staining on wool

3.3.4. Color fastness of the dyed samples

The color fastness characteristics of wool yarn treated at different concentrations of Ag is presented in Table 4. The wash and light fastness of dyed samples with safflower extract was moderate to good (3-4) and (5), respectively. Generally, the wash and light fastness ratings of dyed samples slightly increased in the presence of Ag NPs. The light fastness depends mainly on photooxidation of dyes rather than intermolecular interactions between dyes and fibers [27, 28]. The washing fastness properties in terms of color change are increased up when Ag are used. The insoluble complexes between safflower extract and Ag on woolen yarn are the reason for the improved color fastness rating.

4. Conclusion

The synthesis of silver nanoparticles with flower part of safflower as strong bio-reducers on the wool yarn was performed sucessfully via sustainable green chemistry method. UV-Vis and DLS data showed silver nanoparticles with favorable particle size and stability characteristics can be easily produced by adjusting the extract and Ag ratio. So that, safflower extract and $AgNO_3$ ratio 1:1 had acceptable particle size, and dyeing properties on the wool. It was found that Ag NPs can improve significantly the dyeing ability (14 units), and color fastness of wool dyed with safflower extract (1-2 units).

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