Indian Journal of Fibre & Textile Research
Vol. 43, December 2018, pp. 488-494

Simultaneous *in situ* synthesis of nanosilver and dyeing of polyamide 6 fabric

Vahid Babaahmadi[1], Majid Montazer[1,a], Mansoureh Ghanbarafjeh[1] & Nasrin Samadi[2]
[1]Textile Department, Functional Fibrous Structures & Environmental Enhancement (FFSEE),
Amirkabir University of Technology, Tehran, Iran
[2]Department of Drug and Food Control, Faculty of Pharmacy and Biotechnology Research Center,
Tehran University of Medical Sciences, Tehran, Iran

Received 4 September 2016; revised received and accepted 7 April 2017

In this research, *in situ* synthesis of silver nanoparticles (Ag NPs) has been established in an aqueous solution along with the dyeing of polyamide 6 fabric through a simple chemical reduction method by using silver nitrate ($AgNO_3$), stannous chloride ($SnCl_2$) and cetyltrimethylammonium bromide (CTAB). $SnCl_2$ is used as a reducing agent in synthesis of Ag NPs and also as mordant in the dyeing of polyamide 6 fabric. The formation and distribution of Ag NPs on surface of the fabric are characterized by X-ray diffraction, scanning electron microscope and energy dispersive X-ray. The SEM images indicate the covering of fabric surface with Ag NPs. Loading of Ag NPs on the fabric surface leads to higher color strength and change in colour. The presence of stannous and silver ions also leads to change in the reflectance behaviour of the dyed fabrics. CTAB has antibacterial properties and shows stabilizing effects in synthesis of Ag NPs, which further shows synergistic effect in antibacterial activities of Ag NPs loaded fabrics.

Keywords: C.I. Mordant Blue 3, Dyeing, Eriochrome Blue R, *In situ* synthesis, Nano silver, Polyamide 6

1 Introduction

Researchers have been trying to design new textile products, such as self-clean, antibacterial, comfort and electro conductive textile by application of nanomaterial[1-5]. Various methods have been presented to produce silver nanoparticles (Ag NPs)[6-14]. Reduction of silver ions from silver salt solution to Ag NPs is one of the most common and economical methods[8-16]. *In situ* synthesis of Ag NPs has been reported by researchers in various substrates[17,18]. Stannous chloride ($SnCl_2$) (reducing agent) is generally used in *ex situ* and *in situ* synthesis of Ag NPs in aqueous solution[15]. Also, $SnCl_2$ is used as a mordant in textile dyeing with mordant dyes[16,19], as a chemical agent for increasing silk weight and for identification of presence of gold compounds (turning bright purple in the presence of gold)[20]. Loading of metal nanoparticles on various substrates such as fabric leads to change in appearance and color[21-22]. Mostly, the color changes to brown with lower lightness, as the lower reflectance in visible range decreases the application of the final product. In this regard the metalized fabrics have treated with different dyes to cover the appearance effect of metal to solve the problems[23]. To the best of our knowledge, there is no report published so far on the simultaneous synthesis of Ag NPs through reduction of $AgNO_3$ with $SnCl_2$ on the surface of fabric along with dyeing. This study focuses on the mentioned problem. A new simple technique has been developed for *in situ* synthesis of Ag NPs along with dyeing of polyamide 6 fabric. $SnCl_2$ has been used as a mordant in dyeing and also as a reducing agent in the synthesis of Ag NPs. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), antibacterial activity and color data (L^*, a^* and b^*) are used for characterization of Ag NPs on fabric surface and to investigate the effect of Ag NPs on dyeing properties and fabric appearance.

2 Materials and Methods

2.1 Materials

Polyamide 6 knitted fabric (90 g/m^2) was purchased from Tehran local market. Silver nitrate ($AgNO_3$ extra pure, 99%, Merck Co), cetyltrimethylammonium bromide (CTAB, Merck Co), stannous chloride ($SnCl_2.2H_2O$, Merck Co) and the nonionic detergent (Eriopon OL, ex-Ciba Co) were used to synthesize nanoparticles. Dyeing was performed with Eriochrome Blue R (C. I. Mordant Blue 3) on polyamide 6 fabric.

2.2 Methods

2.2.2 Pre-mordanting of Polyamide 6 Fabric with $SnCl_2$

The purchased fabrics were washed with 1 g/L nonionic detergent at 60 °C for 30 min and then

---

[a]Corresponding author.
E-mail: tex5mm@aut.ac.ir

rinsed with deionized (DI) water to remove the probable contamination on the surface. First of all, to evaluate the isoelectric point, 0.5 g polyamide 6 fabric was stirred in 50 mL $NaNO_3$ solution (0.1 M) for 24 h in different *p*H (from 2 to 11) adjusted by HNO_3 and NaOH. In the next step, the washed fabrics were treated with 3 and 6 % (o.w.f.) $SnCl_2$ at liquor-to-fabric ratio (L:G) of 40:1 and *p*H 6 and then boiled for 45 min. The solution bath was well mixed for uniform absorption of Sn^{2+} ions on the fabric surface. Finally, the fabrics were rinsed and dried at room temperature.

2.2.2 Simultaneous Dyeing and in situ Synthesis of Ag NPs on Polyamide 6 Fabric

The precursor solutions were prepared by adding CTAB into $AgNO_3$ solution while stirring (3500 rpm) for a period of 2 min at room temperature. For preparation of dye-precursor solution, 1% (o.w.f) dye was added to the above precursor solution. [CTAB] to [$AgNO_3$] ratio is the influencing factor to control synthesis process, size of Ag NPs and also dyeing characterization. The pre-mordanted polyamide 6 fabrics were treated with dye precursor solution at L:G = 40:1. The dye-precursor solution was kept in cold condition (T < 10 °C) to decrease the reduction rate before reaction time. The temperature was increased slowly up to 80 °C for the synthesis of nanoparticles and dyeing. The treated polyamide 6 fabrics were washed and dried at room temperature. Different prepared solutions are presented in Table 1.

2.2.3 Characterization of Ag NPs Loaded Polyamide 6 Fabric

Surface morphology of loaded fabrics was investigated by scanning electron microscopy (SEM) applying 30 keV at different magnifications. Hitachi S4160 was also employed for SEM and energy dispersive X-ray (EDX) analysis on some samples. X-ray diffraction (XRD) type 3003pts Seifert Germany (λ=1.54060 A° at 40 kV and 30 mA) with Cu K-α irradiation was used to confirm the formation of silver nanoparticles on the surface of fabric. Also, silver and stannous were quantified by inductively coupled plasma optical emission spectroscopy (ICP - OES).

2.2.4 Color Measurement

The three coordinates (L^*, a^* and b^*) of CIELAB color system were obtained using a color Eye XTH colorimeter. The CIELAB color system is widely used in the color measurement of textile. In this system, L^* shows the lightness of the fabric, whereas a^*, b^* and ΔE indicate red-green, yellow-blue colors and color difference respectively. The color strength value (f_k) is taken as the sum of *K/S* values in the visible region of the spectrum, as shown below:

$$f_k = K\sum_{400}^{700}\left(\frac{k}{s}\right)_\lambda \left(\bar{x}_{10,\lambda}+\bar{y}_{10,\lambda}+\bar{z}_{10,\lambda}\right)$$

where $\bar{x}_{10,\lambda}$, $\bar{y}_{10,\lambda}$ and $\bar{z}_{10,\lambda}$ are the color matching functions for 10° standard observer at each wavelength (ISO 7724/1-1984)[23,24]. Wash fastness of each dyed samples was tested according to AATCC test method 61-2007 (1A) and also to evaluate light fastness, the fabrics were exposed under daylight irradiation (the average daylight intensity was about 58.5 W/m^2) for about 120 h.

2.2.5 Characterization of Antibacterial Activity

Qualitative antibacterial efficiency of synthesis of Ag NPs on polyamide 6 fabric was determined against two bacteria, namely *Staphylococcus aureus* (Gram positive) and *Escherichia coli* (Gram negative) according to a modified version of AATCC test method 147-2004[8]. The average width of a zone of

Table 1—Description of samples with 1% dye and different precursor solutions

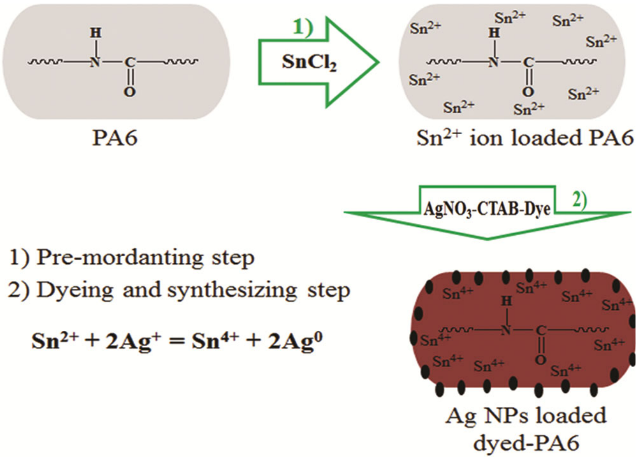
Sample No.	CTAB, g/L	$AgNO_3$, g/L	$SnCl_2$, % (owf)
0 (Control)	0.00	0.00	0
1	0.00	0.00	0
2	0.34		
3	0.68		
4	0.00	0.08	
5	0.17		
6	0.34		
7	0.00	0.17	
8	0.34		
9	0.68		
10	0.00	0.00	3
11	0.34		
12	0.68		
13	0.00	0.08	
14	0.17		
15	0.34		
16	0.00	0.17	
17	0.34		
18	0.68		
19	0.00	0.00	6
20	0.34		
21	0.68		
22	0.00	0.08	
23	0.17		
24	0.34		
25	0.00	0.17	
26	0.34		
27	0.68		

0.17 g/L $AgNO_3$=1mM $AgNO_3$.

inhibition of the test specimens was calculated using the following equation:

$$W = \frac{T - D}{2}$$

where W is the width of inhibition zone (mm); T, the total diameter of test specimen and clear zone; and D, the diameter of test specimen[8].



Scheme 1 — *In situ* synthesis and dyeing of PA6

3 Results and Discussion

3.1 Formation of Ag NPs on Polyamide 6 Fabric along with Dyeing

Preparation of Ag NPs was carried out by a simple method along with dyeing of polyamide 6 fabric. The isoelectric point of polyamide 6 fabric (isoelectric *p*H) was measured at around 5.5 based on the above-mentioned method[25]. According to *p*H of pre-mordanting ($SnCl_2$) bath, Sn^{2+} ions are absorbed on fabric through electrostatic attraction by amide groups or temporary embedded in the inter-fibre and inter-yarns spaces[26,27]. On the other hand, dye molecules are added to the precursor solution containing $AgNO_3$ and CTAB with different ratio to prepare dye-precursor solution. The dye molecules are absorbed on the pre-mordanted fabric surface via stannous ions on the surface. Ag^+ is reduced by stannous ions, keeping Ag^0 attached to the fabric surface within amide chains[15,28], and in this way Sn^{2+} ions are oxidized and produce Sn^{4+} on fabric surface[15]. Ag nuclei are grown and aggregated to produce larger cluster, and eventually Ag NPs are synthesized (Scheme 1).

3.2 X-ray Diffraction and Inductively Coupled Plasma Optical Emission Spectroscopy

The X-ray spectra of the samples are presented in Fig. 1(a), indicating similar spectrum as reported by

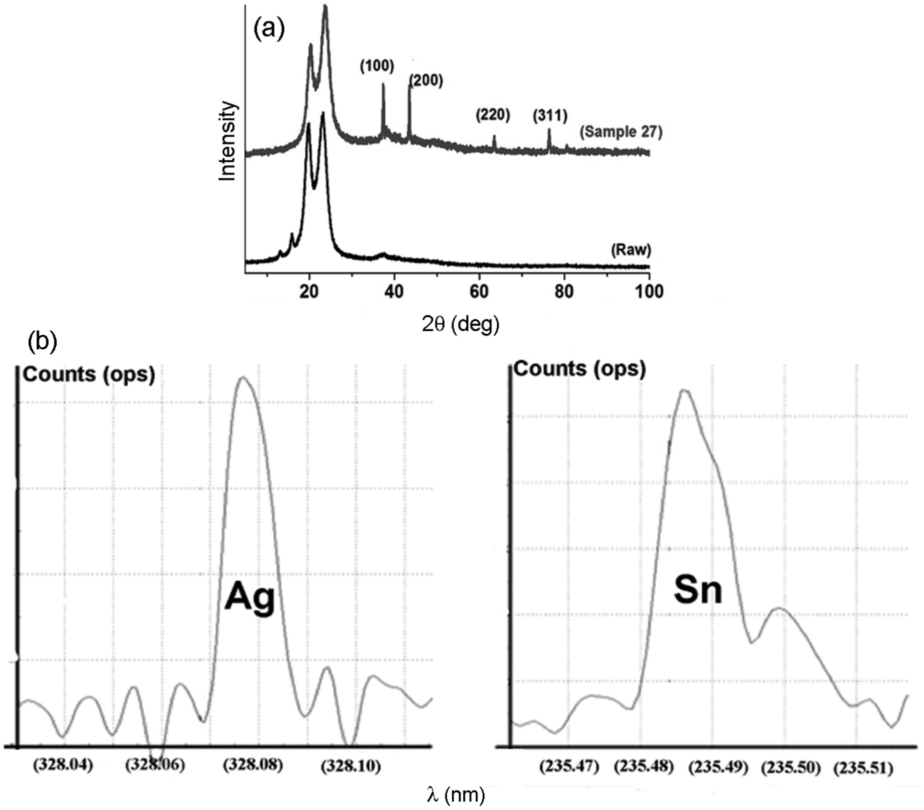


Fig. 1 — XRD spectra of (a) raw and sample 27 and (b) ICP-OES analysis of sample 27

others[29]. As shown in Fig. 1, the diffraction peaks located at about 2θ= 20.1˚ and 24˚ correspond to (200) and (002, 202) reflections of the α-form crystals of the polyamide 6 respectively. All the prominent peaks at 2θ = 38˚, 44.44˚, 64.54˚, 77.38˚, and 81.6° represent (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) Bragg's reflections of fcc structure of silver[15]. Sample 27 shows the XRD pattern of synthesized and dyed fabrics with highest concentration of materials ($SnCl_2$ 6%, $AgNO_3$ 1 mM and [CTAB]/[$AgNO_3$] 4). All intensities of peaks are normalized according to the high intense peak, showing synthesis of Ag crystals on the fabric surface. The crystal size is calculated using Scherrer's equation, indicating an average size of 20 nm. The silver and stannous contents of the treated polyamide fabric (sample 27) are found about 82.36 and 347.3 ppm for Ag (primary wavelength 328.076 nm) and for Sn (primary wavelength 235.485 nm) respectively based on ICP-OES [Fig. 1(b)].

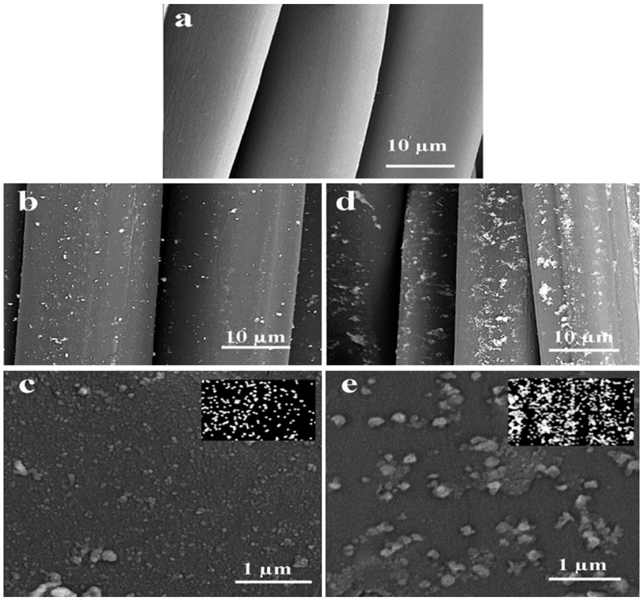
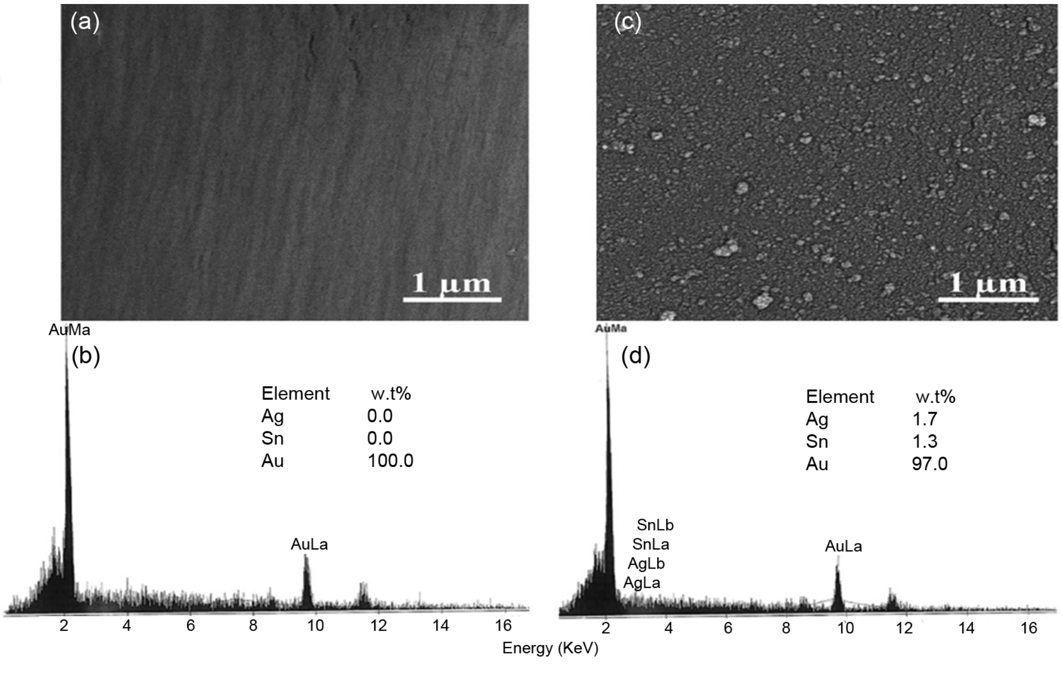


Fig. 2 — SEM images (a) raw, ×2500, (b) sample 17, ×2500, (c) sample 17, ×30000 (inset in Ag map), (d) sample 16, ×2500 and (e) sample 16, ×30000 (inset in Ag map)

3.3 SEM and EDX Study

The SEM images and elemental maps of polyamide 6 fabrics, treated with different materials, are presented in Fig. 2. CTAB acts as a stabilizing agent in synthesis and hence, the precursor solutions with CTAB lead to smaller particles (D < 100 nm) as shown in Figs. 2(b) and (c). Figures 2(d) and (e) show the loading of Ag NPs (D < 300 nm) on fabric surface without CTAB. Presence of dye molecules along with Ag ions in same bath leads to the absorption of Ag ions by dye molecules and then increase of nucleation place in further loading. Also, the synthesized Ag NPs are finally attached to the amide chains or within the polyamide 6 fabric structure. These actions reduce the possible contact between the nanoparticles and prevent further aggregation [Fig. 2(e)]. Figure 3



Element	w.t%
Ag	0.0
Sn	0.0
Au	100.0

Element	w.t%
Ag	1.7
Sn	1.3
Au	97.0

Fig. 3 — SEM images and EDX spectra (a) SEM of raw, ×30000, (b) EDX of raw, (c) SEM of sample 27, ×30000 and (d) EDX of sample 27

shows SEM images and EDX pattern of raw and samples 27 (highest amount of CTAB) at ×30000 magnification. Figures 3(a) and (c) show the effect of CTAB concentration and dye molecules on the size of nanoparticle and the distribution. Increase of CTAB concentration in presence of dye leads to the smaller particle size with narrow distribution. Figures 3(b) and (d) show the EDX spectra of different samples, indicating Ag and Sn on the samples. The EDX spectrum shows the presence of 1.7% Ag and 1.3% Sn on the treated sample.

3.4 Dyeing Characterization

3.4.1 Color Coordinates

The color changes are expressed via CIELAB color coordinates. Figure 4 shows the specific location and lightness of various dyed samples. Figure 4(a) shows the color space diagram and illustrates the position of each dyed sample in the color space. The color coordinates of all samples are changed, indicating higher yellowness. However, a small change is observed in the hue, chroma and lightness. The stannous ions are acting as a mordant responsible for the wavelengths shift and lower reflectance at 400-550 nm. All samples indicate lower greenness and blueness. In other words, most of the samples show higher amount of b* than the original sample. Table 2 shows the color difference between the samples and just dyed sample. The possible reasons are improvement in dye absorption (decrease in reflectance).

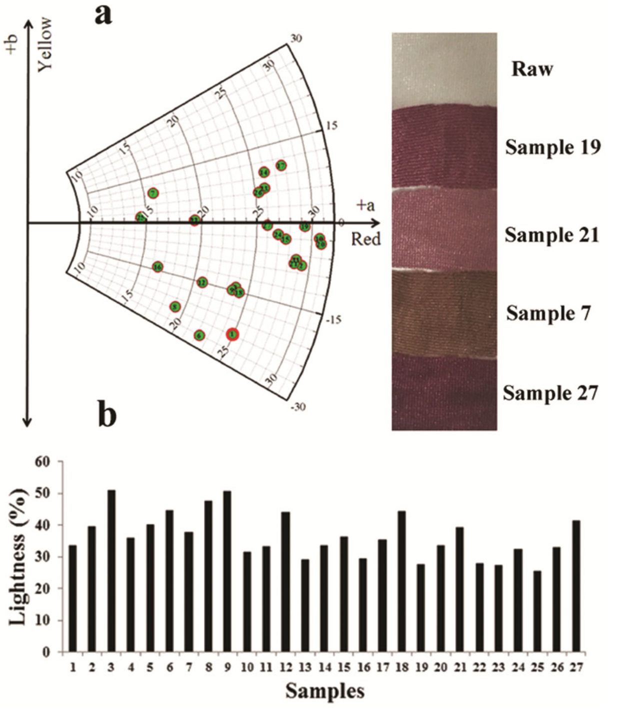


Fig. 4 — Specific location of dyed samples in the color space (a) specific location and card shade and (b) lightness of dyed samples

3.4.2 Color Strength Value (f_k) and Reflectance Data

Presence of metal ions such as Sn and Ag in dyeing leads to change in the absorbance behaviour of dyed fabric. The metal ions make complex with dye, increase the absorbance and also change the peak positions. The color strength of a dye in surface is a measure of its ability to impart color. This property is characterized by the absorption in the visible region (400-700) of the spectrum and can be expressed as a color strength value (fk)[22]. The color strength is also calculated in addition to *K/S* for in-depth investigation. Figure 5 shows *K/S* value of different samples with diverse material ratio at 400-700 nm. Stannous ions make complex with the dye, and fabrics show more absorbance below 600 nm due to more dye absorption. The absorbance increases in the entire visible range, leading to higher color strength. Increase in Sn ions concentration leads to the lower

Table 2 — Color difference (ΔE) and color fastness of different samples

Sample No.	ΔE	Wash fastness		Light fastness
		Staining	Alteration	
1	0.0	4/5	4	3
2	10.6	4/5	4	3/5
3	17.9	4	4/5	3/5
4	20.3	4.0	4	3
5	9.2	4/5	4	3
6	11.2	4/5	4/5	3
7	15.1	4	4/5	3
8	15.0	4	4/5	3
9	17.35	4/5	4/5	3
10	11.8	4/5	4/5	3/5
11	8.8	4/5	4/5	3/5
12	11.5	4	3	3
13	11.6	4/5	3	3/5
14	14.7	4/5	3/5	3
15	10.1	4	4	3
16	9.9	4/5	4	3
17	15.8	4/5	4	3
18	11.3	4/5	4/5	3
19	13.1	4	4/5	3/5
20	11.4	4/5	4/5	3/5
21	10.2	4/5	4/5	3/5
22	12.1	4/5	3	3/5
23	14.7	4/5	3	3
24	9.9	4/5	3/5	3
25	15.5	4/5	3	3/5
26	12.9	4/5	3/5	3/5
27	12.8	4/5	4	3/5

λ_{max} and higher color strength. The color strength for samples 1, 10 and 19 are 170.89, 238.20 and 323.39 respectively. The absorbance and the color strength at 400-470 nm increase in the presence of Ag ions. The color strength for samples 1, 4 and 7 are 170.89, 186.5 and 145.86 respectively. The color strength increases with more Ag ions; leads to lower color strength [Fig. 5(b)]. The Ag ions at high concentration are linked to the ionic parts of the dye and decreases the dye absorption on the fabric. The *K/S* spectrum indicates two peaks related to the dye and metal in presence of Ag. CTAB acts as a levelling agent for anionic dyes in polyamide dyeing[30] and stabilizing agent in nanoparticle synthesis. Figure 5(c) shows the *K/S* spectrum of samples with different concentrations of CTAB. The values of color strength for samples 1, 2 and 3 are 170.89, 70.1 and 52.91 respectively. CTAB possibly connects with chemical bonds to the dye molecules, thus reducing the dye absorption. In presence of both Ag and Sn ions, Ag NPs will be synthesized on the fabric surface. Generally, the color strength of samples increases under this condition, as Ag NPs are synthesized on the fabric surface. The presence of silver nanoparticles on the fabric surface leads to darker color, adsorbing blue range of spectrum. Figure 5(d) shows *K/S* spectrum of different samples. The values of color strength for samples 1, 14 and 17 are 170.89, 210.86 and 183.30 respectively.

3.4.3 Color Fastness

Color fastness refers to the ability of a dyed fabric to retain the original color. The wash and light fastness of the dyed samples are presented in Table 2. Some metals act as a mordant in dyeing process, improving the wash fastness. It seems that this complex is larger than dye molecule trapped in the amide chain physically. Also, the linking between mordant and dye is very important factor for improving the dye fastness. The results for color fastness show good durability of dyed fabrics under washing process and also daylight irradiation in presence of silver nanoparticles.

3.5 Antibacterial Activity

The treated samples were evaluated against Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria based on inhibition zone (Fig. 6). The samples treated with CTAB indicate the high antibacterial activity against *Staphylococcus aureus* according to its outer cell wall (width of inhibition zone is about 6 mm). It seems, CTAB has synergistical effect on Ag NPs against mentioned bacteria. As it is mentioned in SEM result, the particle size decreases in presence of CTAB, thus the releasing rate of Ag ions increases based on large surface area. Also, CTAB is an antibacterial agent which is used in different industry including the textile industry[31].

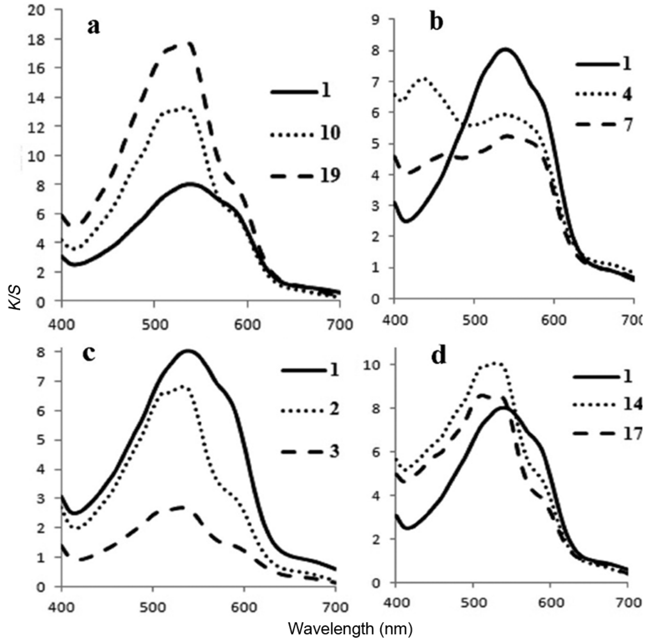


Fig. 5 — *K/S* spectra of different sample in visible range, effect of (a) $SnCl_2$, (b)$AgNO_3$, (c) CTAB and (d) $SnCl_2$, $AgNO_3$, CTAB

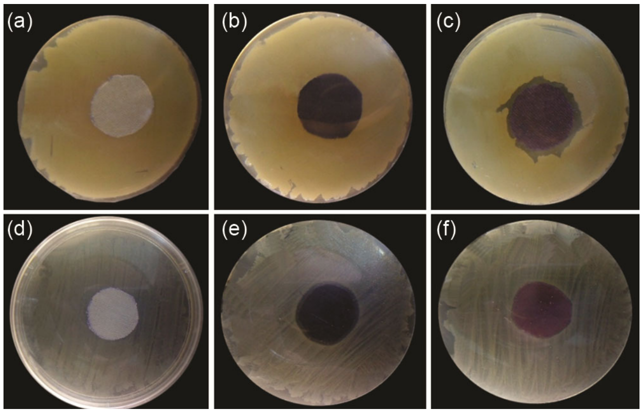


Fig. 6 — Antibacterial properties of different samples against *S aureus* and *E coli* (a) raw *(S aureus)*, (b) sample 25 *(S aureus)*, (c) sample 27 *(S aureus)*, (d) raw *(E coli)*, (e) sample *25 (E coli)* and (f) sample 27 *(E coli)*

4 Conclusion

A novel and simple method is developed to synthesise Ag NPs through *in situ* chemical reduction of $AgNO_3$ with $SnCl_2$ along with dyeing of polyamide 6 fabric. A possible mechanism is proposed to explain the simultaneous formation of Ag NPs along with dyeing of the polyamide 6 fabric by using Sn^{2+} ions as a reducing agent and mordant. The nanometric analysis such as XRD patterns and SEM images show the formation of Ag NPs with crystal size of 20 nm and particle size of about 100 nm on the fabric surface. Increasing Sn ions leads to the higher color strength due to the change in reflectance behaviour and Ag NPs loading through the dyeing process. The antibacterial results against Gram-positive (*Staphylococcus aureus*) bacteria show a good activity on dyed sample. Overall, this research successfully presents a new method for simultaneous synthesis of Ag NPs along with dyeing of polyamide 6 fabric through simple exhaustion method.

References

1 Dawson T, *Color Technol*, 124 (2008) 261.
2 Montazer M & Hashemikia S, *Color Technol*, 128 (2012) 403.
3 Montazer M and Seifollahzade S, *Color Technol*, 127 (2011) 322.
4 Montazer M, Parvinzadeh M & Kiumarsi A, *Color Technol*, 120 (2004) 161.
5 Montazer M, Chizarifar G & Harifi T, *Color Technol*, 130 (2014) 13.
6 Dastjerdi R & Montazer M, *Colloids Surf B*, 81 (2010) 32.
7 Montazer M, Behzadnia A, Pakdel E, Rahimi M K & Moghadam M B, J *Photochem Photobio B*, 103 (2011) 207.
8 Barani H, Montazer M, Samadi N & Toliyat T, *Colloids Surf B*, 92 (2012) 9.
9 Dastjerdi R, M Montazer, Stegmaier T & Moghadam M B, *Colloids Surf B*, 91 (2012) 280.
10 Montazer M, Alimohammadi F, Shamei A & Rahimi M K, *Carbohyd Polym*, 87 (2012) 1706.
11 Dastjerdi R & Montazer M, *Colloids Surf B*, 79 (2010) 5.
12 Montazer M, Alimohammadi F, Shamei A & Rahimi M K, *Colloids Surf B*, 89 (2012) 196.
13 Dastjerdi R & Montazer M, *Colloids Surf B*, 88 (2011) 381.
14 Dastjerdi R & Babaahmadi V, *Colloids surf A*, 386 (2011) 45.
15 Babaahmadi V, Montazer M, *J Text Inst*, 106 (2015) 970.
16 Kumaresan M, Palanisamy P N & Kumar P E, *J Basic Appl Sci Res*, 1 (2011) 933.
17 Barani H, Montazer M, Samadi N & Toliyat T, *Colloids Surf B*, 92 (2012) 9.
18 Allahyarzadeh V, Montazer M, Hemmati Nejad N & Samadi N, *J Appl Polym Sci*, 129 (2013) 892.
19 Wanyama P A G, Kiremire B T, Ogwok P & Murumu J S, *Int Archive Appl Sci Technol*, 1 (2010) 81.
20 Hunt L B, The True tory of Purple of Cassius, *Gold Bulletin*, 9 (1976) 134.
21 Montazer M, Alimohammadi F, Shamei A & Rashidi M K, *Carbohyd Polym*, 87 (2012) 1706.
22 Chattopadhyay D P & Patel B H, *Indian J Fibre Text Res*, 34 (2009) 368.
23 Gorensek M & Recelj P, *Text Res J*, 92 (2009) 138.
24 Baumann W, Groebel B, Krayer M & Oesch H, *J Soc Dyers Color*, 103 (1986) 100.
25 Mustafa S, Dilara B & Nargis K, *Colloids Surf A*, 205 (2002) 273.
26 Akbari A, Remigy J C & Aptel P, *Chem Eng Procc,* 41 (2002) 601.
27 Vankar P S & Shanker R, *Pigm Resin Technol*, 38 (2009) 242.
Montazer M, Mozaffari A & Alimohammadi F, *Fibre Text East Eur*, 23 (2015) 100.
28 Singh N & Khanna P K, *Mater Chem Phys*, 104 (2007) 367.
29 Simoncic B & Kert M, *Dyes Pigm*, 54 (2002) 221.
30 Bagherzadeh R, Montazer M, Latifi M, Sheikzadeh S & Sattari M, *Fibers Polym*, 8 (2007) 368.