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Color shading, color fastness, antibacterial and ultraviolet protection properties of silk fabric colored by silver nanoparticles

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Abstract

This research studied the effects of different factors used in an *in-situ* method for forming colored silver nanoparticles (AgNP) on the properties of silk fabric; namely color shading, color strength, relative unlevelness index, color fastness to washing, antibacterial and UV shielding properties. In addition, improvement with an acrylic binder on color fastness to washing and antibacterial property after 20 cycles of washing of AgNP-treated silk fabric were also investigated. It was found that the optimum condition for treatment by the *in-situ* method was 2.0% owf of silver nitrate ($AgNO_3$) solution, $AgNO_3$ to trisodium citrate ratio at 1:3 (%w/w), exhaustion temperature at 90°C and treatment time at 90 min or 120 min at pH 4.0. The higher concentration of those two factors, the higher the dark brown shade on the AgNP-treated silk fabrics. AgNP-treated silk fabric had a better UV protection than that of the pristine silk fabric. After 20 washes, the color fastness to washing of AgNP-treated silk fabric either with or without acrylic binder coating was rated low. Antibacterial activity against *S. aureus* of AgNP-treated silk fabric without coating acrylic binder decreased to 40% of bacterial reduction, but AgNP-treated silk fabric coated with acrylic binder still had 100% antibacterial property.

1. Introduction

In recent years, the development of nanomaterials, either gold or silver nanoparticles, has become a major focus for the textile researchers due to their abilities to provide simultaneously not only specific beautiful colors but also enhancing functionalities, such as antibacterial, self-cleaning, flame retardancy, hydrophobicity, ultraviolet protection, and so on [1-7]. Gold or silver nanomaterials can provide a new way to produce a color for the textile materials. In addition, these nano-colorants do not require any chromophore for imparting color like traditional synthetic or natural dyestuffs because the coloration of nanomaterials is obtained from their Localized Surface Plasmon Resonance (LSPR) properties. Thus, preparing such nanomaterials for use as colorants avoids leaving a massive amount of chemicals and dyestuffs in the wastewater which needs to be treated before discharging to the environment. There are three methods used for the coloration of nanomaterials on textiles [8]. The first method for coloration is to add the metallic nano-colorants in the process of fiber spinning. This method is suitable for synthetic fibers only because synthetic fiber needs to process via fiber spinning. The second method is to impregnate or exhaust the fiber or fabric with colloidal nano-particles by using the force from the dyeing machine. This second method is similar to the dyeing process with pigment dispersion in textile industry. The second method needed preparation of colloidal nano-colorant before use, of which stability is highly sensitive for coloration of textiles. The third method is *in-situ* synthesis performed by exhausting metal ions into the fiber or fabric and *in-situ* formation of metallic nanoparticles occurred within the fiber or fabric structure by using an appropriate reducing agent. In this study, the third method, *in-situ* synthesis, was selected to generate silver nanoparticles (AgNP) for imparting color on silk fabric.

Silk is a natural protein fiber known as the queen of textile due to its superior properties, such as gloss, smooth texture, soft handle and good drapability. However, the potential defects of silk fabric include less durable press property after laundering, less antibacterial and less resistant to sunlight. It was possible to enhance these defect properties of silk fabric by using anisotropic silver nanoparticles with different LSPR assembled on the silk fabric through electrostatic interaction between nanoparticles and silk fibers. This approach would provide both color shading and antibacterial and UV shielding properties on silk fabric. Previous reports relating to this research are the studies of Hassan and Koyama [8] on the formation of AgNP on acrylic fibers via *in-situ* synthesis formation using trisodium citrate (TSC) as a reducing agent, Mahmud *et al.* [9] on the functionalization of organic cotton fabric with green synthesized AgNP using nontoxic sodium alginate as a reducing agent, Hasan *et al.* [10] on the functionalization of nylon fabric surfaces in terms of excellent coloration and UV protection properties developed by *in-situ* synthesis of chitosan mediated, Shahid *et al.* [11] on producing AgNP via *in-situ* synthesis on silk fabrics using ferulic acid as a reducing agent and Tang *et al.* [12] on the preparation of blue silver nano prisms and red silver nano disk colloids on wool fabric. The treated wool fabric with different anisotropic silver nanoparticles showed different color shading and antibacterial activity against the bacteria of *Escherichia coli*. All the researchers mentioned above had the same conclusions that concentration of silver nitrate ($AgNO_3$), type of reducing agent, pH and time and temperature of treatment affected the color shade because of changing LSPR of AgNP. From the above information, it is interesting to beneficiate the *in-situ* synthesis to small scale textile industry with an application of textile technology. Therefore, in this study, we chose to study the *in-situ* synthesis to make silk fabric having both color and enhanced functionalities, UV shielding and antibacterial at the same time by exhaustion of silver ions into silk fabric and then convert them into colored silver nanoparticles by using TSC as a reducing agent. The effect of $AgNO_3$ concentration, concentration of $AgNO_3$ to TSC ratio, temperature treatment, time treatment and pH of $AgNO_3$ solution on color shade change, color strength (K/S), relative unlevelness index (RUI), antibacterial activity and UV transmission through AgNP-treated silk fabrics were reported in this study. In addition, nanostructures of silver on the silk fabrics treated at different condition of *in-situ* synthesis of AgNP were investigated as well by using scanning electron microscope (SEM).

2. Materials and methods

2.1 Materials

Bleached silk woven fabric (warp yarn count 20-22/3D amount of 96 filament/inch, weft yarn count 27-29/6D amount of 78 filament/inch) were purchased from Natural Niche Co., Ltd. Silver nitrate ($AgNO_3$, 99.5%) was purchased from S.M. Chemical Supplied Co., Ltd. Tri-sodium citrate 2-hydrate (TSC) as a reducing agent was purchased from M&P Impex Ltd. Acrylic binder (UKAPRINT NF-505) was purchased from V.P.C. group. All chemicals used in this study were purchased from the companies located in Thailand.

2.2 *In-situ* synthesis of AgNP on silk fabric

Incorporation of AgNP on silk fabrics via *in-situ* synthesis were carried out in the laboratory dyeing machine. The study on coloration of silk fabrics via *in-situ* synthesis of AgNP was divided into two parts.

The first part was to study the effect of concentration of $AgNO_3$, ratios of $AgNO_3$ and TSC, temperature and time of treatment on color shade reported as CIE L*a*b*, K/S and RUI. The procedure for coloration of silk fabric was as follows: a piece of 4 g of bleached silk fabric was immersed in the $AgNO_3$ solution at three different percent weights on fabric (%owf) of 1, 1.5 and 2 %owf from 1% $AgNO_3$ stock solution, using 1:100 material to liquor ratio. After that, the mixture was raised from room temperature to 60°C or 90°C at a rate of 5°C·min^{-1} and held at each temperature for 15 min. Then TSC from 1% stock solution at three different ratios of $AgNO_3$ to TSC at 1:1, 1:2 and 1:3 (%w/w) was dropped in to $AgNO_3$ solution. The step of reduction with TSC was kept either at 60°C or 90°C for 60, 90 and 120 min. At the end of treatment, the AgNP-treated silk fabrics were rinsed with deionized water several times and dried at 60°C in the oven for 60 min.

The second part was to study the pH effect on color shade change, K/S and RUI. The initial pH of silver nitrate solution was 5.6 in the first part of this study. For the second part, the pH of $AgNO_3$ solution was adjusted to pH 4 with 0.1 M CH_3COOH aqueous solution and adjusted to pH 8 with 0.1 M NaOH aqueous solution in the selected treatment conditions of *in-situ* synthesis of AgNP on silk fabric. The results of color shade, K/S and RUI on the AgNP-treated silk fabric were investigated to select the appropriate treatment condition from the first part for further study in the second part. In addition, AgNP-treated silk fabrics studied in the second part were evaluated not only color shade, K/S and RUI but also the antibacterial and ultraviolet shielding properties and color fastness to washing. The morphologies of silk fabrics before and after coloration with AgNP were studied as well.

2.3 Color measurements

The CIE L*a*b* values of untreated and AgNP-treated silk fabrics were measured using a Macbeth Color-Eye 7000A spectrophotometer. Samples were measured under illuminant D65, using a 10° standard observer and specular included. The colorimetric analysis of CIE L*a*b*, which L* is lightness from black to white (0 to 100), a* is shade from red to green ratio (+/-) and b* is shade yellow to blue ratio (+/-). The CIE L*a*b* values implied the color shade of material. The color strength (K/S) value was also obtained by the same instrument by measure the reflectance (%R) at specific wavelength and calculated the K/S value by equation 1 below. Whereas R is the reflectance value.

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

2.4 Levelness evaluation

Relative unlevelness index (RUI) was used for the evaluation of the color levelness on AgNP-treated silk fabric. RUI was calculated through the reflectance values of twenty randomly selected spots on AgNP-treated silk fabric samples within the visible wavelength between 400 nm to 700 nm with data taken at 10 nm intervals by using Macbeth Color-Eye 7000A spectrophotometer which set the parameters for measurement at illuminant D65 light source, a 10° standard observe with specular included. The RUI was calculated in Equation (2). Whereas S_λ is the standard deviation of reflectance value at each wavelength. R is the mean of reflectance value of n measurement of each wavelength [12]. RUI interpretation values are listed in Table 1.

$$RUI = \sum_{\lambda=400}^{700} S_\lambda / R \tag{2}$$

Table 1. Relative unlevelness index (RUI) interpretation [12].

Visual Appearance of Levelness	RUI
Excellent levelness (unlevelness not detectable)	< 0.2
Good levelness (noticeable unlevelness under close examination)	0.2-0.49
Poor levelness (apparent unlevelness)	0.5-1.0
Bad levelness (conspicuous unlevelness)	> 1.0

2.5 Colorfastness

The color fastness to washing of the untreated and AgNP-treated silk fabrics with and without acrylic binder coating was measured according to ISO 105-C01 Color Fastness to Washing. The condition used for testing was done under time and temperature at 40°C for 30 min with standard soap solution at liquor ratio 50:1. The color change of those silk fabrics was evaluated by using gray scales having the rating 1 to 5. The rating of 5 is the excellent rating while 1 is the poorest rating. For the acrylic binder treatment condition, the AgNP-treated silk fabric incorporated with silver nanoparticles was immersed in the solution of acrylic binder at 100 $g \cdot L^{-1}$ for 5 min and then padded through the padder machine for controlling the % wet pickup around 70% to 80%, after that cured the fabric at 130°C for 3 min before testing the colorfastness.

2.6 Surface morphologies

The surface morphologies of untreated and treated AgNP-treated silk fabrics were investigated by using Filed Emission Scanning Electron Microscopy (FE-SEM) technique. Those silk fabric surfaces were scanned using a JEOL JSM-7610F having Schottky field emission gun providing high resolution at an accelerated voltage of 10 kV with conductive coating.

2.7 UV transmission

The untreated and treated AgNP-treated silk fabric samples were determined by the UV transmittance using a Perkin Elmer Lambda 35 UV/VIS spectrophotometer. Measurement attachment was used to assess the percent transmission (%T) of light pass through the silk fabrics at wavelength in the range of 200 nm to 400 nm. Each sample was measured five times at different positions. The average of the data obtained from 5 measurements was used for the value of %T. In addition, the average UV transmittance in the UVA region ($T(UVA)_{av}$) was also calculated. Normally, the %T was implied to the ability of UV protection. The less %T and the lower $T(UVA)_{av}$ indicated the better UV protection. Not only the UV transmission can tell the UV protection, but the Ultraviolet Protection Factor (UPF value) can also as well. UPF value [13] was calculated as equation below. Whereas E_λ is the solar spectral irradiance, S_λ is the Erythemal spectral effectiveness, T_λ is the spectral transmittance of fabric, and Δ_λ is the wavelength interval.

$$\mathrm{UPF} = \frac{\sum_{280\ \mathrm{nm}}^{400\ \mathrm{nm}} E\lambda \times S\lambda \times \Delta\lambda}{\sum_{280\ \mathrm{nm}}^{400\ \mathrm{nm}} E\lambda \times S\lambda \times \Delta\lambda \times T\lambda} \quad (3)$$

2.8 Antibacterial activity

The antibacterial activities of the untreated and AgNP-treated silk fabrics were evaluated according to the AATCC test method 100-2004, screening against *Staphylococcus aureus* (ATCC 6538) as representative of Gram-positive bacteria. The antibacterial activities of the tested fabric samples were analyzed by the quantitative method of counting microbial colony forming units (CFU) of *Staphylococcus aureus.* The percent reduction of bacteria is calculated as the following Equation (4).

$$R = \frac{(B-A)}{B} \times 100 \quad (4)$$

Whereas R is the reduction percentage of microbial colonies. A is the number of microbial colonies remaining on the agar plate with treated silk fabric for 24 h contact time. B is the number of microbial colonies remaining on the agar plate for control at 0 h contact time.

3. Results and discussion

3.1 CIE $L^*a^*b^*$, color strength (K/S) and RUI values

CIE $L^*a^*b^*$, K/S and RUI values of the AgNP-treated silk fabrics coloring with different treatment conditions by varying $AgNO_3$ solution at three different %owf of 1, 1.5 and 2 %owf at pH 5.6 and three different ratios of $AgNO_3$ to TSC of 1:1, 1:2 and 1:3 (%w/w) with treatment temperature at 60°C and 90°C and treatment time at 60, 90 and 120 min are reported in Table 2-3, respectively.

3.1.1 Effect of treatment temperature

The color shade of the AgNP-treated silk fabrics coloring with various treatment conditions of $AgNO_3$ at pH 5.6 from 1, 1.5 and 2 %owf with three different ratios of $AgNO_3$ to TSC of 1:1, 1:2 and 1:3 (%w/w) at treatment time for 60, 90 and 120 min with treatment temperature at 60°C as reported in Table 2 was almost colorless or very pale grayness. The K/S of AgNP-treated silk fabrics was also low. It could be concluded that the treatment temperature at 60°C was not appropriate to drive the reduction of $AgNO_3$ to Ag nanoparticles to occur even at severe treatment condition adjusted to 2%owf of $AgNO_3$ concentration with ratio of $AgNO_3$ to TSC at 1:3 (%w/w) at treatment time for 120 min. For RUI values, AgNP-treated silk fabrics coloring with the above treatment conditions with treatment temperature at 60°C had high RUI values which mean that the color shade on the AgNP-treated silk fabrics was apparent unlevelness. However, when changing the treatment temperature to 90°C instead of 60°C, the color shade on the AgNP-treated silk fabrics was started to notice from the very pale grayness to deep yellowish brown depending on concentration of $AgNO_3$, $AgNO_3$ to TSC ratio and treatment time used for *in-situ* method for synthesis AgNP. The results of CIE $L^*a^*b^*$, K/S and RUI values of the AgNP-treated silk fabrics colored with those factors with treatment temperature at 90°C are reported in Table 3 which were discussed further below.

3.1.2 Effect of $AgNO_3$ concentration

According to the results reported in Table 3, the color shade of the AgNP-treated silk fabrics turned from bright white for untreated silk fabric to very pale greyish, light yellowish brown to deep yellowish brown when increasing the $AgNO_3$ up to 2.0%owf. The lightness value (L^*) decreased from 86.84 for untreated silk fabric to 49.88 for AgNP-treated silk fabric coloring with 2%owf of $AgNO_3$ solution. In addition, the K/S also increased up to 11.55 with increasing the concentration of $AgNO_3$ up to 2.0%owf. It could be concluded that changing the concentration of $AgNO_3$ could produce various color shade and color strength on the AgNP-treated silk fabrics. For the

RUI values reported in Table 3, the RUI values of AgNP-treated silk fabrics coloring with 1% or 1.5%owf of $AgNO_3$ were varied in the range from 0.74 to 0.50 or 0.82 to 0.50, respectively. These ranges of RUI values indicated that the visual appearance of color shade on AgNP-treated silk fabrics was poor levelness. While the RUI values of AgNP-treated silk fabrics colored with 2%owf of $AgNO_3$ were varied in the range from 0.80 to 0.39 interpretated that the levelness of color shade on AgNP-treated silk fabrics was changed from the poor levelness to good levelness. It could be concluded that the levelness of color shade on AgNP-treated silk fabrics could be improved by adjusting the $AgNO_3$ concentration along with other factors such as ratios of $AgNO_3$ to TSC, treatment time and treatment temperature.

3.1.3 Effect of $AgNO_3$ to TSC ratios

The AgNP-treated silk fabrics colored with three different levels of $AgNO_3$ to TSC ratios incorporated with %owf of $AgNO_3$ lower than 2%owf had very pale grayness as reported in Table 3. The CIE L*a*b* values were not much different from each other under those condition treatments. The color shade and K/S of AgNP-treated silk fabrics were changed conspicuously with an increase $AgNO_3$ to TSC ratio from 1:1 to 1:3 (%w/w) incorporated with 2%owf of $AgNO_3$. The color shade reported as CIE L*a*b* of AgNP-treated silk fabrics turned from light grayness to light yellowish brown and deep yellowish brown with an increase the $AgNO_3$ to TSC ratio to 1:3 (%w/w). Increasing the $AgNO_3$ to TSC ratio also provided higher K/S on the AgNP-treated silk fabrics. For RUI value, RUI decreased with an increase in the $AgNO_3$ to TSC ratio. It was implied that the levelness of color shade on AgNP-treated silk fabric could be improved by adjusting $AgNO_3$ to TSC ratio to 1:3 (%w/w) instead of 1:1 or 1:2 (%w/w).

3.1.4 Effect of treatment time

The color shade of the AgNP-treated silk fabrics turned from light yellowish brown to deep yellowish brown when increasing the treatment time. The deepest shade of yellowish brown was achieved when the treatment time was 120 min. The K/S and RUI values as reported in Table 3 could be concluded that treatment time for 120 min provided the high K/S value and good levelness with low RUI value of AgNP-treated silk fabrics.

According to the results of color shade (CIE L*a*b*), high K/S and good levelness (RUI) reported in Tables 2-3, it was found that the suitable conditions for treatment by *in-situ* method for coloring silk fabric with AgNP were 2%owf of $AgNO_3$, $AgNO_3$ to TSC ratio at 1:3 and treatment temperature at 90°C for treatment time of 60, 90, and 120 min. These treatment conditions with the different pH at 4, 5.6 and 8 were selected to study further for effect of pH on color shade (CIE L*a*b*), K/S and RUI values of the AgNP-treated silk fabrics.

Table 2. CIE L*a*b*, K/S and RUI values of the AgNP-treated silk fabrics at various treatment conditions with treatment temperature at 60°C.

Sample	$AgNO_3$ concentration (%owf)	$AgNO_3$ to TSC ratios	Time (min)	pH	L*	a*	b*	K/S value	RUI value
Control	0	-	-	-	86.84	-0.44	3.29	0.30	-
Ag1-1-60M		1:1	60	5.6	78.29	2.32	8.91	0.47	1.07
Ag1-1-90M	1.0	1:1	90	5.6	81.11	1.91	10.34	0.52	1.05
Ag1-1-120M		1:1	120	5.6	83.48	0.96	8.36	0.52	0.98
Ag1-2-60M		1:2	60	5.6	81.92	1.09	7.75	0.46	1.01
Ag1-2-90M		1:2	90	5.6	83.62	0.89	8.97	0.46	0.91
Ag1-2-120M		1:2	120	5.6	83.82	0.79	8.99	0.48	0.85
Ag1-3-60M		1:3	60	5.6	83.36	0.53	5.68	0.45	0.98
Ag1-3-90M		1:3	90	5.6	82.95	0.76	7.85	0.48	0.88
Ag1-3-120M		1:3	120	5.6	84.02	0.69	8.13	0.51	0.82
Ag1.5-1-60M		1:1	60	5.6	81.89	1.75	9.48	0.49	1.01
Ag1.5-1-90M	1.5	1:1	90	5.6	82.32	1.44	9.38	0.50	0.93
Ag1.5-1-120M		1:1	120	5.6	83.27	0.91	8.89	0.51	0.91
Ag1.5-2-60M		1:2	60	5.6	82.69	1.23	7.79	0.47	0.83
Ag1.5-2-90M		1:2	90	5.6	82.33	0.83	8.45	0.48	0.76
Ag1.5-2-120M		1:2	120	5.6	82.26	1.40	9.42	0.50	0.74
Ag1.5-3-60M		1:3	60	5.6	82.27	1.04	7.52	0.52	0.72
Ag1.5-3-90M		1:3	90	5.6	81.42	0.76	8.18	0.55	0.64
Ag1.5-3-120M		1:3	120	5.6	80.06	0.90	8.92	0.58	0.60
Ag2-1-60M		1:1	60	5.6	78.02	3.72	12.80	0.62	0.91
Ag2-1-90M	2.0	1:1	90	5.6	80.45	2.42	11.57	0.63	0.81
Ag2-1-120M		1:1	120	5.6	80.42	2.03	10.75	0.68	0.76
Ag2-2-60M		1:2	60	5.6	81.08	1.79	11.61	0.62	0.90
Ag2-2-90M		1:2	90	5.6	79.76	2.28	12.27	0.67	0.80
Ag2-2-120M	2.0	1:2	120	5.6	79.69	2.18	12.00	0.73	0.77
Ag2-3-60M		1:3	60	5.6	81.43	1.55	10.81	0.68	0.83
Ag2-3-90M		1:3	90	5.6	82.14	1.20	10.19	0.73	0.77
Ag2-3-120M		1:3	120	5.6	80.74	1.57	10.31	0.81	0.75

Table 3. CIE L*a*b*, K/S and RUI values of the AgNP-treated silk fabrics at various treatment conditions with treatment temperature at 90°C.

Sample	$AgNO_3$ concentration (%owf)	$AgNO_3$ to TSC ratios	Time (min)	pH	L*	a*	b*	K/S value	RUI value
Control	0	-	-	-	86.84	-0.44	3.29	-	-
Ag1-1-60M		1:1	60	5.6	80.17	1.11	6.87	0.49	0.74
Ag1-1-90M	1.0	1:1	90	5.6	78.86	1.16	6.84	0.57	0.51
Ag1-1-120M		1:1	120	5.6	77.89	1.28	6.60	0.59	0.50
Ag1-2-60M		1:2	60	5.6	79.03	0.99	7.51	0.51	0.72
Ag1-2-90M		1:2	90	5.6	77.92	1.13	7.06	0.61	0.66
Ag1-2-120M		1:2	120	5.6	77.81	1.08	7.04	0.63	0.51
Ag1-3-60M		1:3	60	5.6	78.82	1.26	7.20	0.55	0.68
Ag1-3-90M		1:3	90	5.6	77.82	1.34	6.33	0.63	0.57
Ag1-3-120M		1:3	120	5.6	76.10	1.06	7.26	0.70	0.50
Ag1.5-1-60M		1:1	60	5.6	78.01	1.66	7.36	0.58	0.82
Ag1.5-1-90M	1.5	1:1	90	5.6	75.56	1.76	7.09	0.70	0.77
Ag1.5-1-120M		1:1	120	5.6	74.02	1.98	7.10	0.75	0.63
Ag1.5-2-60M		1:2	60	5.6	76.07	1.90	8.07	0.71	0.65
Ag1.5-2-90M		1:2	90	5.6	72.95	2.49	8.43	0.77	0.55
Ag1.5-2-120M		1:2	120	5.6	68.61	3.66	8.64	0.95	0.50
Ag1.5-3-60M		1:3	60	5.6	73.23	1.78	8.61	0.74	0.64
Ag1.5-3-90M		1:3	90	5.6	71.33	2.88	8.45	0.82	0.51
Ag1.5-3-120M		1:3	120	5.6	68.67	3.63	8.86	0.96	0.50
Ag2-1-60M		1:1	60	5.6	72.18	2.92	8.25	0.84	0.80
Ag2-1-90M	2.0	1:1	90	5.6	65.99	4.83	10.26	1.20	0.65
Ag2-1-120M		1:1	120	5.6	61.07	6.78	15.80	1.65	0.49
Ag2-2-60M		1:2	60	5.6	65.83	5.40	12.60	1.24	0.68
Ag2-2-90M		1:2	90	5.6	56.31	8.09	26.17	3.63	0.41
Ag2-2-120M	2.0	1:2	120	5.6	53.97	9.10	31.45	5.90	0.39
Ag2-3-60M		1:3	60	5.6	66.21	5.14	12.10	4.97	0.51
Ag2-3-90M		1:3	90	5.6	52.49	9.26	28.81	6.85	0.49
Ag2-3-120M		1:3	120	5.6	49.88	11.36	38.34	11.55	0.42

3.1.5 Effect of pH

The effect of pH on color shade reported as CIE L*a*b*, K/S and RUI values of the AgNP-treated silk fabrics were reported in Table 4. The silk fabric treated at pH 4 with 2%owf of $AgNO_3$, $AgNO_3$ to TSC ratio at 1:3 (%w/w) had deepest color with the highest K/S of 12.45, 17.62 and 18.17 at different exhaustion times of 60, 90 and 120 min, respectively. The treatment solutions at pH 8 produced the lowest K/S on the AgNP-treated silk fabrics. While the treatment solutions at pH 5.6 produced the K/S in the middle between those at pH 4 and pH 8. In addition, the CIE L* a* b* values of the AgNP-treated silk fabrics at pH 4 showed the lowest lightness value (L*) and highest values of a* and b* which implied that the AgNP-treated silk fabrics at pH 4 had the deeper yellowish brown than those at pH 5.6 or pH 8. Therefore, pH 4 was the optimum pH for the coloration of the silk fabric with AgNP. Figure 1 shows the color shade of AgNP-treated silk fabrics colored with 2.0%owf of $AgNO_3$, $AgNO_3$ to TSC ratio at 1:3 (%w/w) and exhaustion temperature at 90°C for 60, 90 and 120 min. It could be concluded that the treatment solution at pH 4 with exhaustion time at 120 min provided the deepest color shade compared with other exhaustion time and other pHs. For the RUI value, all those of the AgNP-treated silk fabrics could be noticeable unlevelness under close examination. However, the levelness of color of the AgNP-treated silk fabrics could be improved by increasing the exhaustion time. It is evident that increasing the exhaustion time from 60 min to 120 min could decrease the RUI value of the AgNP-treated silk fabrics from 0.51 to 0.32. It was implied that the color levelness of AgNP-treated silk fabrics was better when the RUI value was lower.

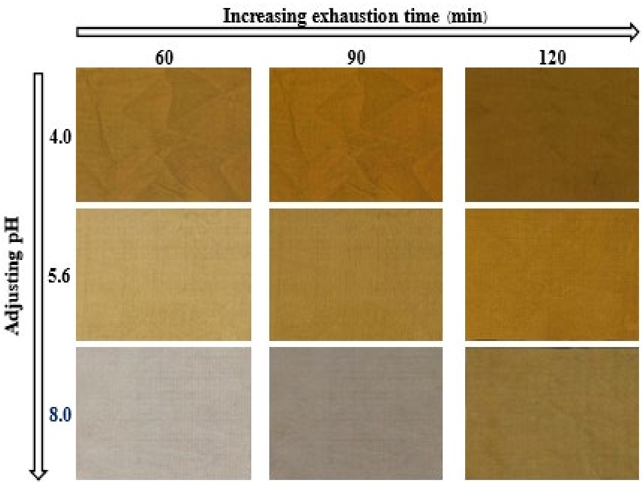

Figure.1 Color palette of the AgNP-treated silk fabrics colored with 2%owf of $AgNO_3$, $AgNO_3$ to TSC ratio at 1:3 (%w/w) with treatment temperature at 90°C at different exhaustion time and pH.

Table 4. CIE L*a*b*, K/S and RUI values of the AgNP-treated silk fabrics by adjusting the pH.

Sample	Time (min)	pH	L*	a*	b*	K/S value	RUI value
Control	-	-	86.84	-0.44	3.29	0.259	-
Ag2-pH4-60M	60	4.0	48.54	12.57	37.11	12.458	0.51
Ag2-pH4-90M	90	4.0	43.08	15.16	38.08	17.625	0.36
Ag2-pH4-120M	120	4.0	42.03	15.12	39.79	18.171	0.32
Ag2-pH5.6-60M	60	5.6	66.21	5.14	12.10	4.965	0.51
Ag2-pH5.6-90M	90	5.6	58.49	7.26	22.81	6.848	0.49
Ag2-pH5.6-120M	120	5.6	49.88	11.36	38.34	11.548	0.42
Ag2-pH8-60M	60	8.0	68.59	4.15	8.57	0.729	0.61
Ag2-pH8-90M	90	8.0	66.13	5.06	10.40	1.286	0.49
Ag2-pH8-120M	120	8.0	56.96	7.76	28.91	4.552	0.45

3.2 Surface morphologies

Surface morphologies of untreated silk fabric and AgNP-treated silk fabrics colored by treatment conditions of 2%owf of $AgNO_3$ at pH 4, 5.6, 8, $AgNO_3$ to TSC ratio at 1:3 (%w/w) at treatment temperature for 90°C with different treatment time for 60, 90 and 120 min. were characterized by FE-SEM to observe the assembly of AgNP deposited on the silk fabric surface as shown in Figures 2-4, respectively. The SEM images of untreated silk fabric (Figures 2(a), Figures 3(a), and Figures 4(a)) shows smooth surface, while the surfaces of AgNP-treated silk fabrics colored at pH 4 with different treatment time for 60, 90 and 120 min as shown in Figure 2(b-d) had sphere-shaped AgNP deposited on the silk fabrics after treatment. Figure 2(d) displays the SEM image of AgNP on silk fabric treated by *in situ* method at pH 4 with treatment time for 120 min having numerous small nano-particles distributed on the surface more than those obtained from other treatment times (60 min and 90 min). The average particle sizes calculated by using Image J program of the AgNP synthesized via *in situ* method at pH 4 were around 83 nm for 120 min treatment time, 103 nm for 90 min treatment time and 106 nm for 60 min treatment time. The SEM images of AgNP deposited on the silk fabrics treated at pH 5.6 as shown in Figure 3 also displayed spherical nanoparticles of silver of the fabric surface. In addition, the 120 min treatment time provided a larger quantity of nanoparticles observed on the silk fabric surface than those of treatment time for 90 min or 60 min as well. The average particle sizes of the AgNP synthesized by *in situ* method at pH 5.6 were around 118 nm for 120 min treatment time, 141 nm for 90 min treatment time and 168 nm for 60 min treatment time. While AgNP deposited on the silk fabrics colored at pH 8 as shown in Figure 4 were larger spherical nanoparticles than those obtained from pH 4 or pH 5.6. The average particle sizes of the AgNP synthesized by *in situ* method at pH 8 were around 139 nm for 120 min treatment time, 160 nm for 90 min treatment time and 225 nm for 60 min treatment time. From the results of SEM characterization, it could be concluded that the optimum condition for treatment by *in-situ* method to obtain homogeneous distribution of numerous small silver nanoparticles on silk fabric was 2%owf $AgNO_3$ at pH 4, $AgNO_3$ to TSC ratio at 1:3 (%w/w) with treatment temperature at 90°C for 120 min treatment time. This optimum treatment condition also provided the deepest color shade on AgNP-treated silk fabric as seen in color palette as shown in Figure 1.

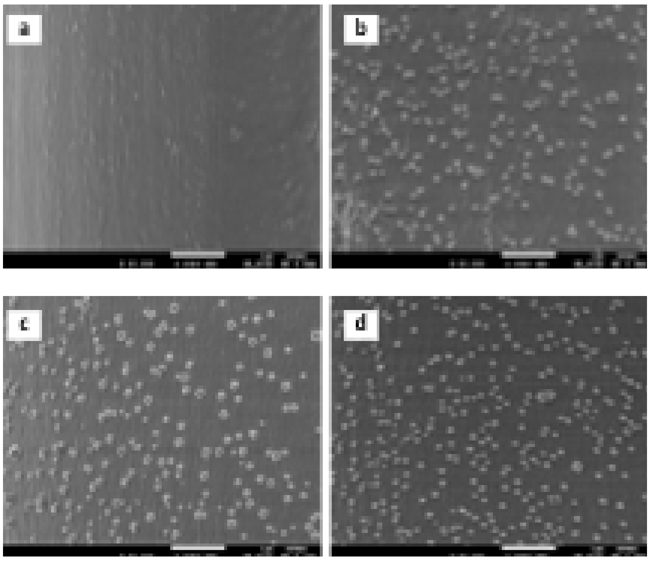

Figure 2. FE-SEM photographs of (a) untreated silk fabric, AgNP-treated silk fabrics at pH 4 with (b) 60 min treatment time, (c) 90 min treatment time and (d) 120 min treatment time.

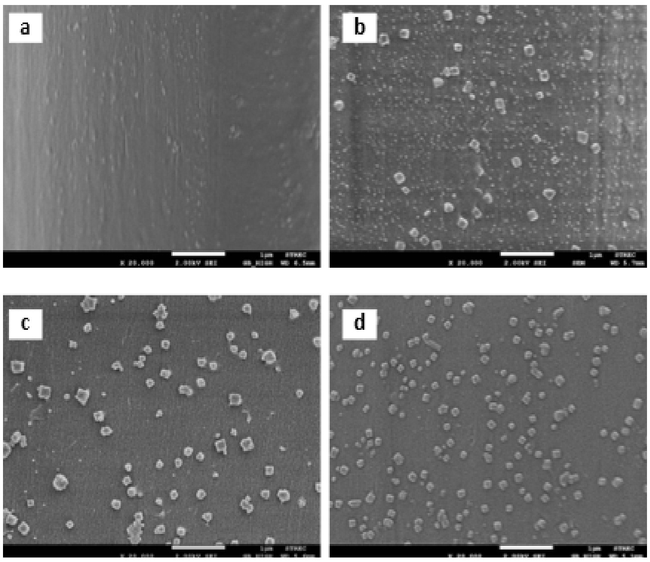

Figure 3. FE-SEM photographs of (a) untreated silk fabric, AgNP-treated silk fabrics at pH 5.6 with (b) 60 min treatment time, (c) 90 min treatment time and (d) 120 min treatment time.

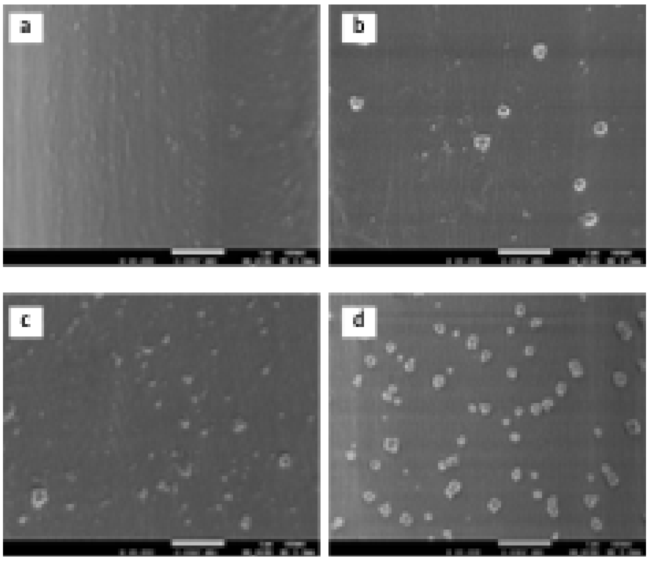

Figure 4. FE-SEM photographs of (a) untreated silk fabric, AgNP-treated silk fabrics at pH 8 with (b) 60 min treatment time, (c) 90 min treatment time and (d) 120 min treatment time.

3.3 UV transmission through the silk fabrics

UV radiation levels are divided into three regions consisting of UV-A (320 nm to 400 nm), UV-B (290 nm to 320 nm) and UV-C (200 nm to 290 nm). Figures 5-7 display UV transmission of the AgNP-treated silk fabrics colored with 2.0 %owf of $AgNO_3$, $AgNO_3$ to TSC ratio at 1:3 (%w/w) treatment temperature at 90°C for 60, 90,120 min treatment time under three different pH of 4, 5.6 and 8, respectively. It was evident that AgNP-treated silk fabrics having AgNP deposited on the surface of silk fabric could reduce the UV transmission. The untreated silk fabric showed UV transmission around 15% to 20% at wavelengths in the zone of UV-A and UV-B, while the AgNP-treated silk fabrics reduced UV transmission to around 5% in those two UV zones. For the pH effect, the AgNP-treated silk fabric colored at pH 4 showed lower %transmittance than those of AgNP-treated silk fabrics colored under either pH 5.6 or pH 8. In addition, the UV transmission decreased with an increase in treatment time. For the $T(UVA)_{av}$ results, the untreated silk fabric had $T(UVA)_{av}$ 19.20%. The $T(UVA)_{av}$ values of the AgNP-treated silk fabrics colored at pH 4 with treatment temperature at 90°C different treatment time at 60, 90 or 120 min were 3.58, 3.22 and 2.71, respectively. While the $T(UVA)_{av}$ values of the AgNP-treated silk fabrics colored at pH 5.6 or pH 8.0 with the same treatment temperature and time were 5.02%, 3.92% and 3.09% for pH 5.6 and 5.70%, 4.52% and 3.44% for pH 8. It could be seen that the AgNP-treated silk fabrics colored at lower pH and treated at longer time had the value of $T(UVA)_{av}$ lower than those of higher pH and shorter treatment time. It was implied that the AgNP-treated silk fabrics colored at lower pH and treated at longer time provided better UV protection for the silk fabric. According to the overall results of UV transmission and value of $T(UVA)_{av}$, it could be concluded that the AgNP-treated silk fabrics had an excellent UV protection capability or less UV transmission than that of untreated silk fabric.

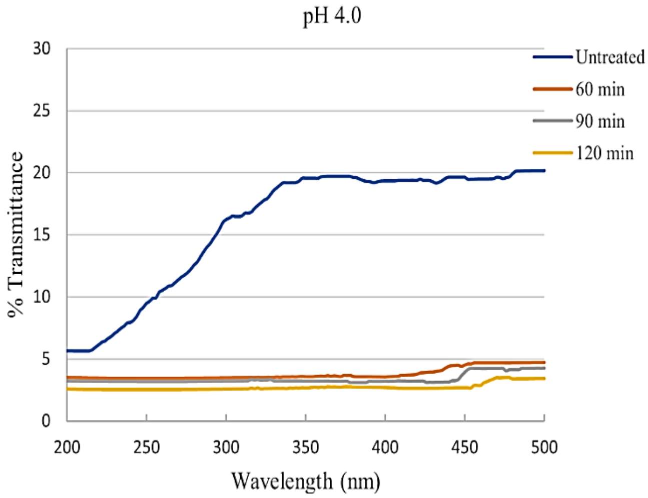

Figure 5. UV transmittance through the AgNP-treated silk fabrics colored with 2.0 %owf of $AgNO_3$ at pH 4, $AgNO_3$ to TSC ratio at 1:3 (%w/w) and treatment temperature at 90°C with treatment time for 60, 90 and120 min.

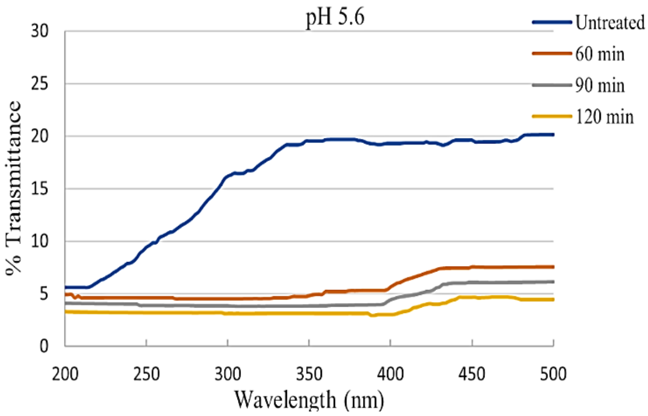

Figure 6. UV transmittance through the AgNP-treated silk fabrics colored with 2.0 %owf of $AgNO_3$ at pH 5.6, $AgNO_3$ to TSC ratio at 1:3 (%w/w) and treatment temperature at 90°C with treatment time for 60, 90 and120 min.

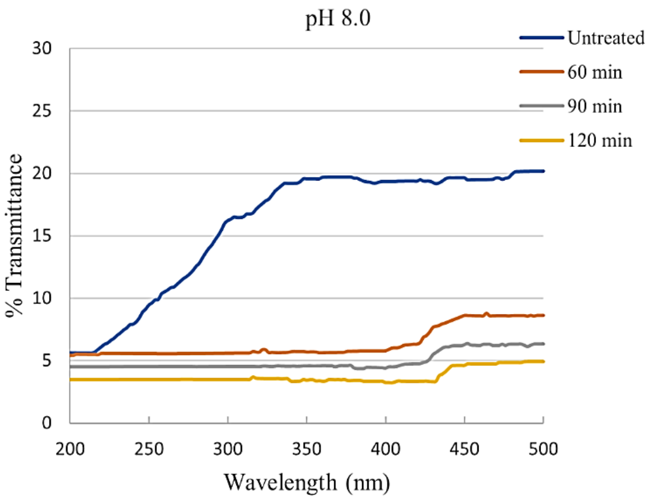

Figure 7. UV transmittance through the AgNP-treated silk fabrics colored with 2.0 %owf of $AgNO_3$ at pH 8, $AgNO_3$ to TSC ratio at 1:3 (%w/w) and treatment temperature at 90°C with treatment time for 60, 90 and120 min.

For the UPF value, the UPF of the untreated silk fabric was 11.85 indicating the low ability to protect the UV. The UPF values of AgNP-treated silk fabrics colored at pH 4 with treatment temperature at 90°C different treatment time at 60, 90 or 120 min were 37.28, 38.32 and 38.82, respectively. The UPF values of AgNP-treated silk fabrics colored at pH 4 were in the range 25 to 39 which indicated that these treated silk fabrics had ability to protect the UV radiation almost 95% as mentioned in the paper of A Khan *et al.* [13]. While the UPF values of the AgNP-treated silk fabrics colored at pH 5.6 or pH 8.0 with the same treatment temperature and time were 12.60, 15.63 and 19.62 for pH 5.6 and 10.77, 13.49 and 17.64 for pH 8. It could be concluded that the AgNP-treated silk fabrics colored at higher pH 4 had the ability to protect UV less than those of pH 4.

According to the results of color shade, K/S, RUI and UV protection of the AgNP-treated silk fabrics as discussed above, it could be concluded that the colorated silk fabric with AgNP by *in-situ* method using the treatment condition of 2.0% owf of $AgNO_3$ at pH 4, $AgNO_3$ to TSC ratio at 1:3 (%w/w) with treatment temperature at 90°C for 120 min treatment time showed the good results of those four properties. Therefore, AgNP-treated silk fabrics synthesized at this optimum treatment condition were used for testing the color fastness and antibacterial property before washing and after 20 cycles of washing. In addition, AgNP-treated silk fabrics synthesized at this treatment condition were finished with the acrylic binder at 3% with 70% to 80% wet pick-up, and then cured at 130°C for 90 min were taken to test the color fastness to washing and antibacterial property to determine the efficiency of acrylic binder as well.

3.4 Color fastness to washing

The results of color fastness to washing in gray scale rating of AgNP-treated silk fabrics coated with or without acrylic binder are shown in Table 5. The acrylic binder coated on the AgNP-treated silk fabrics provided a better color fastness to washing than those of uncoated AgNP-treated silk fabric after first-five cycles of washing. The AgNP-treated silk fabrics coated with acrylic binder still had the color fastness to washing in gray scale rating at 3 after 10 cycles of washing and gray scale rating at 2 after 15 cycles of washing, while the AgNP-treated silk fabrics without coating acrylic binder had the color fastness to washing in gray scale rating at 1 only after 10 cycles of washing. It was implied that the AgNP-treated silk fabrics coated with acrylic binder had more durability of colorfastness to washing than that of the AgNP-treated silk fabrics without acrylic binder coating. The self-crosslinking of acrylic binder occurred on AgNP-treated silk fabric could entrap AgNP more tightly inside the structure of AgNP-treated silk fabric. This phenomenon could enhance the color fastness to washing for AgNP-treated silk fabrics coated with acrylic binder.

3.5 Evaluation of antibacterial activity

The pristine silk and silk fabrics colored with AgNP were tested antibacterial activity by counting microbial colony forming units (CFU) value of gram-positive bacteria (*S. aureus*). The tested results found that

0 h 24 h (0% reduction)

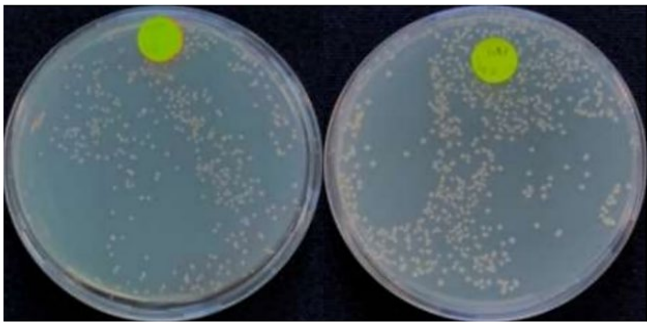

Figure 8. Evaluation of antibacterial activity of pristine silk fabric at 0 h and 24 h contact time.

without washing with 20 cycles of washing

0 h 24 h (100% reduction) 0 h 24 h (40% reduction)

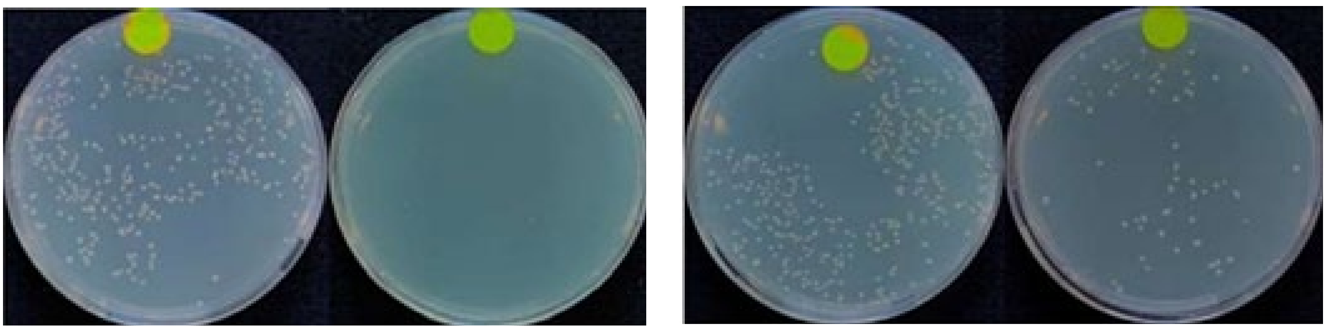

Figure 9. Evaluation of antibacterial activity on AgNP-treated silk fabrics without acrylic binder coating at 0 h and 24 h contact time both before washing and after 20 cycles of washing.

Table 5. Colorfastness to washing of the uncoated and coated AgNP-treated silk fabrics with acrylic binder.

Sample	Number of cycles of washing								
	0	1	2	3	4	5	10	15	20
AgNP-treated silk fabrics without acrylic binder	5	4/5	3/4	3	3	2	1	1	1
AgNP-treated silk fabrics with acrylic binder	5	4/5	4/5	4/5	4/5	4/5	3	2	1

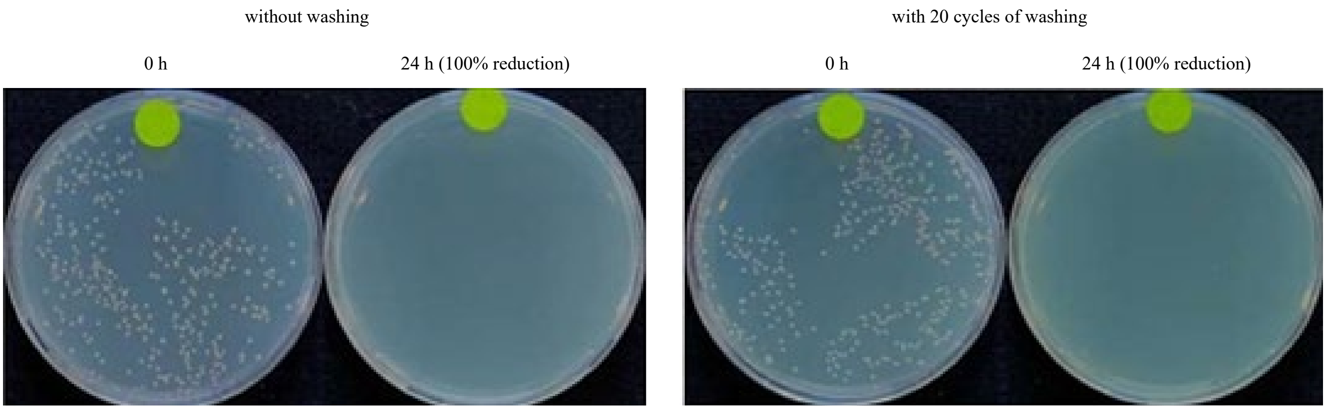

Figure 10. Evaluation of antibacterial activity on AgNP-treated silk fabrics with acrylic binder coating at 0 and 24 h contact time both before washing and after 20 cycles of washing.

the agar plates for pristine silk fabrics were full of bacteria colonies after contact time both 0 h and 24 h, which informed that the pristine silk fabric has no antibacterial property as shown in Figure 8. While the agar plates for the silk fabric colored with AgNP without acrylic binder coating and without washing were found that the agar plate for contact time at 0 h was full of bacteria colonies. On the contrary, no colonies of bacteria were found on the agar plate of the silk fabric colored with AgNP after contact time at 24 h as shown in Figure 9. It proves that the AgNP treated silk fabric without acrylic binder coating and without washing has antibacterial property. In this study, the antibacterial durability was also studied by testing 20 cycles of consecutive washing. The AgNP treated silk fabric without acrylic binder coating with 20 cycles of washing had antibacterial activity against *S. aureus* decreased to 40% of bacteria reduction after 24 h contact time as shown in Figure 9. The AgNP-treated silk fabric without acrylic binder coating did not show much antibacterial durability. This was because the antibacterial property of AgNP-treated silk fabric without acrylic binder coating was reduced more than a half after 20 cycles of washing. To improve the antibacterial durability, the AgNP-treated silk fabric was coated with the acrylic binder at 3% and cured at 130°C for 90 min. The AgNP-treated silk fabrics coated with acrylic binder had almost 100% of bacterial reduction at 24 h contact time both before washing and 20 cycles of washing as shown in Figure 10. It means that the acrylic binder could improve the antibacterial durability on the AgNP-treated silk fabrics.

4. Conclusions

Silk fabrics were colored by *in-situ* method for forming the AgNP at various treatment conditions by adjusting concentration of $AgNO_3$, $AgNO_3$ to TSC ratio, pH and treatment time and temperature. The effects of different factors used in the *in-situ* method for forming colored AgNP on the properties of color shading, K/S, RUI, color fastness to washing, antibacterial and UV protection on the AgNP-treated silk fabrics were evaluated in this study. The results found that the optimum condition for treatment by the *in-situ* method was 2.0 %owf of $AgNO_3$, $AgNO_3$ to TSC ratio at 1:3 (%w/w), treatment temperature at 90°C and treatment time at 90 min or 120 min in acidic condition at pH 4.0. The results of AgNP-treated silk fabric obtained at the optimum condition showed that the color shading turned from bright white to light yellowish-brown and to deep yellowish-brown depending on the concentration of $AgNO_3$ and $AgNO_3$ to TSC ratio. The higher concentration of those two factors, the higher the dark brown shade on the AgNP-treated silk fabric. Moreover, temperature and time of treatment in the *in-situ* method also help to improve the deepness of color shade and decrease RUI value. The more RUI value decreased, the better the levelness of color shade on the AgNP-treated silk fabrics. The AgNP-treated silk fabric had a better UV protection than that of the untreated silk fabric. In addition, the acrylic binder coating on the AgNP-treated silk fabrics could enhance the antibacterial durability and color fastness to washing of the AgNP-treated silk fabrics after 20 cycles of washing.

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References

[1] A. K. M. A. Asif, and M. Z. Hasan, "Application of nanotechnology in modern textiles: A review," *International Journal of Current Engineering and Technology,* vol. 8, pp. 227-231, 2018.

[2] M. Rafique, I. Sadaf, M. S. Rafique, and M. B. Tahir, "A review on green synthesis of silver nanoparticles and their applications," *Artificial Cells, Nanomedicine, and Biotechnology*, vol. *45*, pp. 1272-1291, 2017.

[3] S. U. Islam, B. S. Butola, and F. Mohammad, "Silver nanomaterials as future colorants and potential antimicrobial agents for natural and synthetic textile materials," *RSC Advances,* vol. 50, pp. 44232-44247, 2016.

[4] A. S. Kupiec, D. Malina, Z. Wzorek, and M. Zimowska, "Influence of silver nitrate concentration on the properties of silver nanoparticles," *Micro & Nano Letters*, vol. 6 pp. 656-660, 2011.

[5] F. M. Kelly, and J. H. Johnston, "Colored and functional silver nanoparticle wool fiber composition," *ACS Applied Material and Interfaces*, vol. 3, pp. 1083-1092, 2011.

[6] H. B. Ahmed, H. E. Emam, H. M. Mashaly, and M. Rehan, “Nanosilver leverage on reactive dyeing of cellulose fibers: Color shading, color fastness and biocidal potentials,” *Carbohydrate Polymers,* vol. 186, pp. 310-320, 2018.

[7] Z. Zhang, X. Lv, Q. Chen, and J. An, “Complex coloration and antibacterial functionalization of silk fabrics based on noble metal nanoparticles,” *Journal of Engineered Fibers and Fabrics,* vol. 14, pp. 1-8, 2019.

[8] M. M. Hassan, and K. Koyama, “Multifunctional acrylic fibers prepared via in-situ formed silver nanoparticles: Physicochemical, UV radiation protection, and antistatic properties,” *Dyes and Pigments,* vol. 159, pp. 517-526, 2018.

[9] S. Mahmud, N. Pervez, H. H. Liu, M. A. Taher, and K. Mohiuddin, “Multifunctional organic cotton fabric based on silver nanoparticles green synthesized from sodium alginate, *Textile Research Journal*, vol. 90, pp. 1224-1236, 2020.

[10] K. M. F. Hasan, H. Wang, S. Mahmud, M. A. Jahid, M. Islam, W. Jin, and C. Genyang, “Colorful and antibacterial nylon fabric via in-situ biosynthesis of chitosan mediated nanosilver,” *Journal of Materials Research and Technology,* vol. 9, pp. 16135-16145, 2020.

[11] M. Shahid, Y. Zhou, X.W. Cheng, M. S. Zar, G. Chen, and R. C. Tang, “Ferulic acid promoted in-situ generation of AgNPs @silk as functional colorants,” *Journal of Cleaner Production*, vol. 176, pp. 736-744, 2018.

[12] A. Y. L. Tang, C. H. Lee, Y. Wang, and C. W. Kan, “Dyeing properties of cotton with reactive dye in nonane nonaqueous reverse micelle system,” *ACS Omega*, vol. 3, pp. 2812-2819, 2018.

[13] A. Khan, A Nazir, A. Rehman, M. Naveed, M. Ashraf, K. Lqbal, A. Basit, and H. S. Maqsood, “A review of UV radiation protection on humans by textiles and clothin,” *International Journal of Clothing Science and Technology*, vol. 32, pp. 869-890, 2020.