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Research Article

Enhanced Antibacterial and Flame Retardant Properties of Silk Fabric by Silver Colloid and Montmorillonite

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Abstract: Silver colloid in blue color was synthesized by a chemical reduction method using $NaBH_4$ as a reducing agent. The silk fabric was dyed with the silver colloid, which was adjusted pH value to 4-5 by adding dropwise acetic acid. The dyeing process was performed by varying time (60-120 min) and temperature (30-100 °C). In addition, the effect of montmorillonite particles adding on flame retardant properties of the silk fabric was investigated. The dyed silk fabrics were characterized for microstructure and color by scanning electron microscope and UV/vis spectrophotometry. Moreover, antibacterial activity against *Staphylococcus aureus* and flame-retardant properties after treated with montmorillonite were examined. It was obtained that the optimum dyeing condition for enhancing the antibacterial property of silk fabric was dyed with silver colloids (pH 4-5) at 100 °C for 90 minutes. In addition, treating with 1 wt% montmorillonite could improve the flame retardant property of the dyed silk fabric.

Keywords: Silver colloid, Antibacterial, Montmorillonite, Flame retardant

1. Introduction

In recent years, silver nanoparticles (AgNPs) have attracted considerable attention due to their exceptional optical and electrical properties, including antibacterial activity, high resistance to oxidation, and high thermal conductivity. AgNPs can be utilized for medical and chemical applications, water treatment, and reducing bacteria on textile fabrics [1,2]. AgNPs can be facile synthesized by a chemical reduction method by using sodium borohydride ($NaBH_4$) as a reducing agent to convert the Ag^+ to $Ag^{0,}$ which ultimately performs antibacterial activity [3,4]. Colorful silver colloids have been applied for textiles coloration with simultaneously enhanced antibacterial properties, including cotton [5], wool [6,7], and silk [8]. For coloration, adjusting pH values of silver colloid to suit the surface charge of textile before the coloring process is significant. For example, silver colloids at pH 4-5 were used for dyeing silk yarns [9].

Recently, many works have focused on enhancing the flame retardant behavior of textiles, especially cotton, which is the most important natural textile fiber widely used in textile applications, using chemical modification [10,11]. However, the usual methods' limitations are that the gas released from halogenated flame retardant is dangerous to human bodies and the environment. Moreover, the use of boron-containing flame retardant for the unwashed fabric is restricted due to its lack of durability [12,13]. Thus the development of an environmentally friendly and effective process to flame retardant finishing of textiles was greatly concerned. Montmorillonite (MMT) is an inorganic mineral clay considered an environmentally benign material, and it does not perform an undesired harmful effect in animals or humans [14]. It was reported that the introduction of MMT clay could improve the flammability, thermal and mechanical properties of the cotton fabric without deterioration those properties [15]. Therefore, the flame retardant study of MMT applied to textile fiber has attracted much attention in recent years [15,16].

In the present work, the multifunctionalization of silk fabrics by using silver colloid and montmorillonite to enhance antibacterial activity and flame-retardant properties are designed. The *Staphylococcus aureus*, a gram-positive bacterium, usually acts as a commensal of the human microbiota. Still, it can become an opportunistic pathogen, a common cause of skin infections including abscesses, respiratory infections such as sinusitis, and food poisoning [17]. In addition, *S. aureus* can survive well on fabrics. Thus, the prepared silk fabrics' antibacterial activity against *S. aureus* was studied. Based on our knowledge, the enhanced antibacterial activity of silk fabrics dyed with AgNPs and treated with MMT has not yet been reported.

2. Experimental

2.1 Materials

$AgNO_3$ was purchased from SRL chemicals. Trisodium citrate (≥99%) and sodium borohydride (≥99%) were purchased from Sigma-Aldrich. Acetic acid (≥99%) and hydrogen peroxide (30 wt%) were purchased from Merck.

2.2 Preparation of Silver colloids

Silver colloid was prepared according to a modified literature method [18,19]. 200 mL of silver nitrate (0.2 mM), 3.6 mL of tri-sodium citrate dehydrate (100 mM), and 0.48 mL of hydrogen peroxide were mixed for 10 min. Afterward, 0.8 mL (100 mM) of sodium borohydride solution was added to the mixture while stirring. The mixture was stirred at room temperature for 1 h, and a silver colloid with blue colors was obtained.

2.3 Preparation of silk fabrics dyed with silver colloids

Silver colloid was adjusted the pH value to 4-5 by adding dropwise of acetic acid. The dyeing process under magnetic stirring was performed by varying time (60-120 min) and temperature (30-100 °C), then it was dried at room temperature.

2.4 Preparation of montmorillonite suspension

Montmorillonite (MMT) suspension (1 wt%) was prepared by suspending 1 g of MMT in 100 mL deionized water under magnetic stirring for 1 h, then sonicated for another 1 h.

2.5 Preparation of silk fabrics treated with montmorillonite

The silk fabrics dyed with silver colloid were immersed for 1 h in MMT suspension (1 wt%) and squeezed to 100% wet pick-up using the pad-dry-cure method at constant pressure. The silk fabrics treated with MMT were dried at room temperatures, followed by curing at 100 °C for 1 min to fix the as prepared MMT on the surface of silk fabrics.

2.6 Characterizations

Silver colloids' UV/vis absorption spectra were obtained using a UV/vis spectrophotometer (Lambda35, PerkinElmer instrument). The morphology of silk fabrics dyed with silver colloid and treated with MMT was observed using a field emission scanning electron microscope (FESEM, JEOL JSM-7001F). The flame retardant property was evaluated by following a Vertical Flammability Test Method (16 CFR.1615 and 1616 [20] and ASTM standard D3659 [21]). The sample size used for testing was 3½ inch × 10 inch. The test samples were placed in separated metal holders and suspended each holder vertically in the test cabinet. Then the sample was burned from the bottom edge by the flame originating from methane gas (the flame length is about 1.5 inch) for 3 s. After that, the char length of each sample was measured.

Antibacterial activity was evaluated according to JIS Z 2801:2010 test method [22], which was performed using a sample with 50 cm × 50 cm in size. The testing conditions are shown in Table 1.

Table 1 Antibacterial testing conditions

Microorganisms	Method	Incubation conditions	Inoculum/Sample
Staphylococcus aureus	JIS Z 2801 : 2010	37 °C, dark, 90% humidity, 24 h	0.4 mL/5×5 cm^2

Antibacterial activity was expressed in terms of calculating percent reduction of bacteria by following formula (1):

$$R = \frac{(B - A) \times 100}{B} \quad (1)$$

where R = % Reduction
A = Log CFU per milliliter of viable bacteria after treatment (24 h)
B = Log CFU per milliliter of viable bacteria before treatment (0 h)

3. Results and discussion

3.1 Coloration and characterization of silk fabric with silver colloid

Blue silver colloids were prepared by chemical reduction method using $NaBH_4$ as a reducing agent. The initial (pH = 7) color of the prepared silver colloid sample in Figure 1(a) with added $NaBH_4$ (0.8 mL) as a reducing agent was in blue. After adding acetic acid to adjust the pH value of the prepared silver colloid, it is visibly evident that the color changes to violet and dark blue when the pH value was adjusted to 4 (Figure 1(b)) and 5 (Figure 1(c)), respectively.

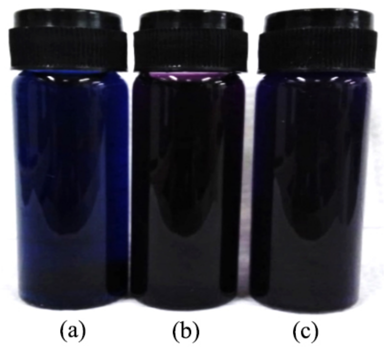

Figure 1 The photographs of the prepared silver colloids (a) with was adjusted pH value to 4 (b) and 5 (c).

Figure 2 shows the UV/vis absorption spectra of the prepared blue silver colloid, which was adjusted pH value to 4-5 by adding dropwise acetic acid. The center of bands shifted from 605 nm (initial) to 530 nm (pH = 5) and 555 nm (pH = 4). The change in the center of bands was assigned to the change in the localized surface plasmon resonance (LSPR) properties which can change the absorption and scattering properties of AgNPs. It can be tuned by controlling the particle size, shape, and the local refractive index near the particle surface of AgNPs [23-25].

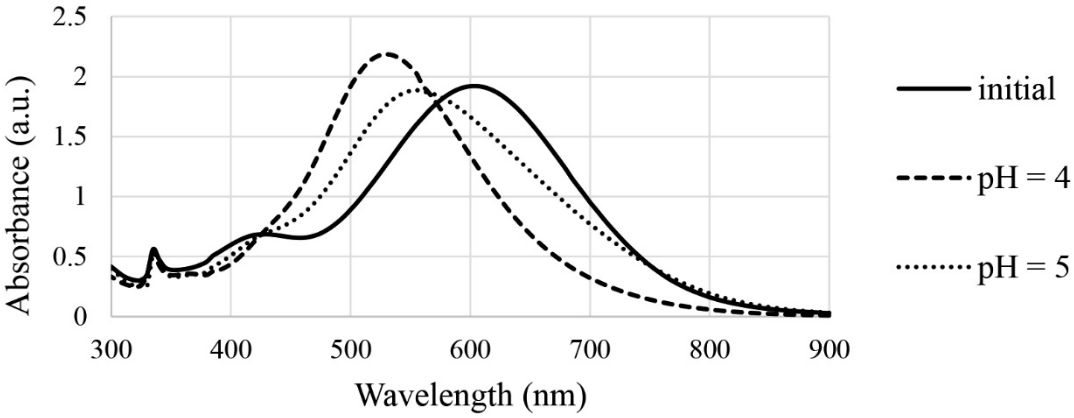

Figure 2 UV/vis absorption spectra of the initial blue silver colloids (pH 7) and after adjusted pH value to 4 and 5.

Figure 3 shows photographs of the silk fabrics before and after dyed with silver colloids which was adjusted the pH value to 4 and 5. It was found that silk fabrics could not be dyed with initial blue silver colloids (pH = 7). The color of the silk fabric remained the same as the original. After adjusting the pH of colloids to 4 and 5, the silk fabric's color was changed from original (Figure 3(a)) to violet (Figure 3(b)) and blue (Figure 3(c)), respectively.

It was demonstrated that adjusting the pH value of the silver colloid was significant for the dyeing of the silver colloid on silk fabric. Silk fabric is an amphoteric substance containing both positive and negative charges depending on environment pH. At acid conditions (pH about 4-5), silk fabric has a positive charge. In contrast, AgNPs in colloid have a negative surface charge, the electrostatic attraction between opposite surface charges resulting in effective silver colloid coloration on silk fabric. The reason for that why at acid condition (pH = 4-5) the silk fabric has a positive surface charge (NH_3) is because of the amino group (–NH_2) of the silk fabric can absorb H^+ from acetic acid. On the other hand, at pH above 5, silk fabric and AgNPs have the same negative surface charge, the repulsion between them restricted the color dyeing process [7,9].

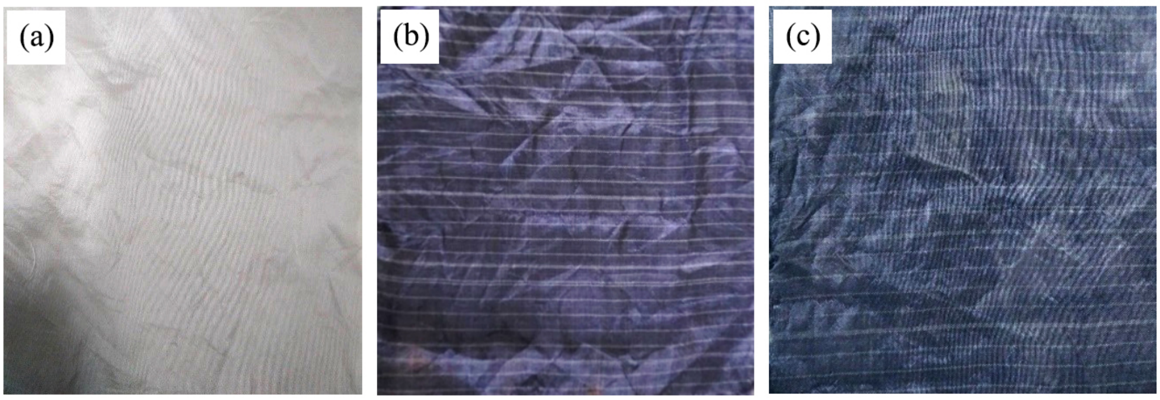

Figure 3 Photographs of the silk fabrics before (a) and after dyed with silver colloid, which was adjusted pH value to 4 (b) and 5 (c).

Figure 4 demonstrates the decrease in a maximum absorbance (770 nm) of initial silver colloids (adjusted pH at about 4-5), and colloids remained after the dyeing process at 100 °C for 0, 60, 90, and 120 min. It was found that the maximum absorbance at 770 nm of silver colloids decreased as dying time increased, which was close to 0 after 90 min. This indicated that AgNPs in colloids were adsorbed and coated onto silk fabric completely at 90 min of the dyeing process. No AgNPs remained in the colloids.

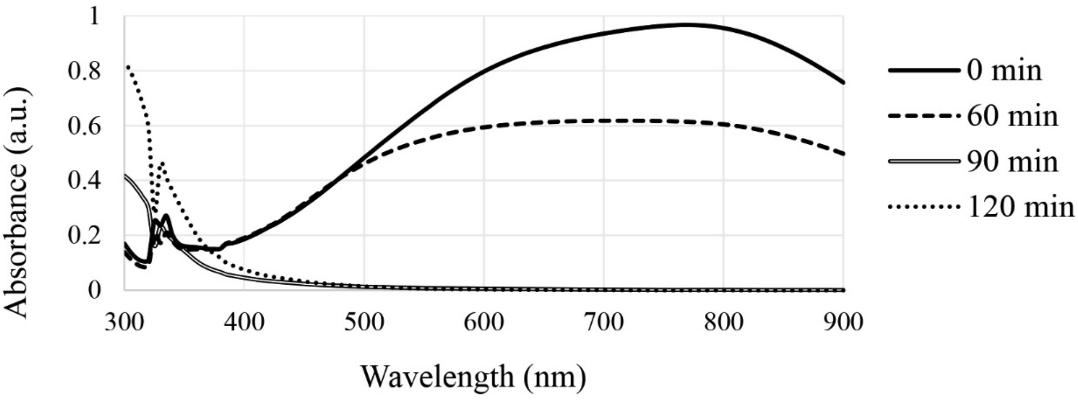

Figure 4 UV/vis absorbance spectra of silver colloids after dyeing at 100 °C for 0, 60, 90, and 120 min.

Figure 5 performs the effect of the dyeing temperature of silver colloids on silk fabric. It was shown that the maximum absorbance (660 nm) of silver colloid was decreased from 0.8 to 0.4, 0.2, and 0 as dyeing temperature increased from the initial (room temperature) to 30, 60, and 100 °C, respectively. The decrease of absorbance indicates that the amount of AgNPs in colloidal decreases, which was coated onto silk fabric. It can be suggested that the optimum condition for enhanced dyeing efficiency of silver colloids on silk fabric was at temperature 100 °C for 90 min.

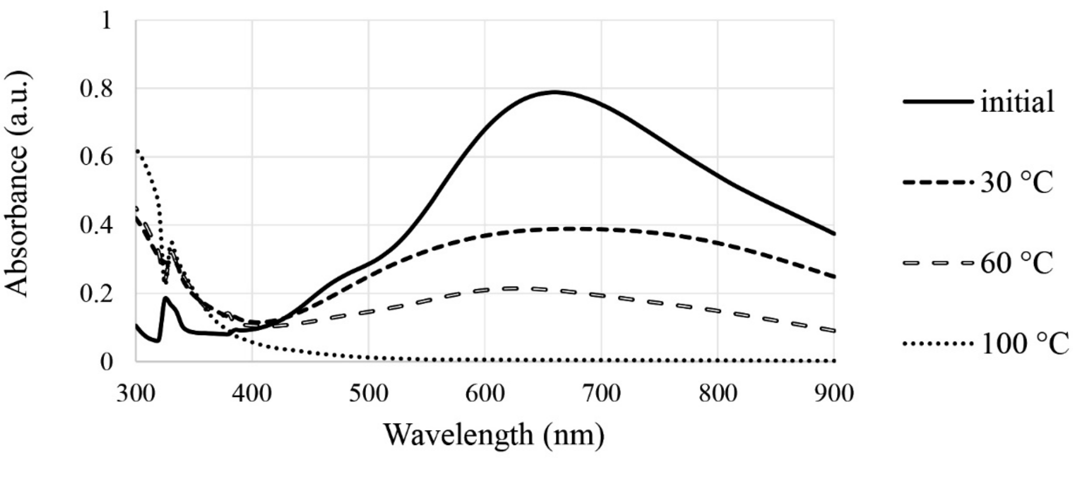

Figure 5 UV/vis absorbance spectra of silver colloids remaining after dyeing at 30, 60, and 100 °C for 90 min compared to initial silver colloid at room temperature.

Figure 6, a scanning electron microscopy (SEM) observation, shows that the surface of undyed silk fabric was clean and smooth, while the silk dyed with AgNPs and treated with MMT had a rougher surface. The change in the surface roughness of silk fabric after dyeing caused by AgNPs and MMT deposition can be seen.

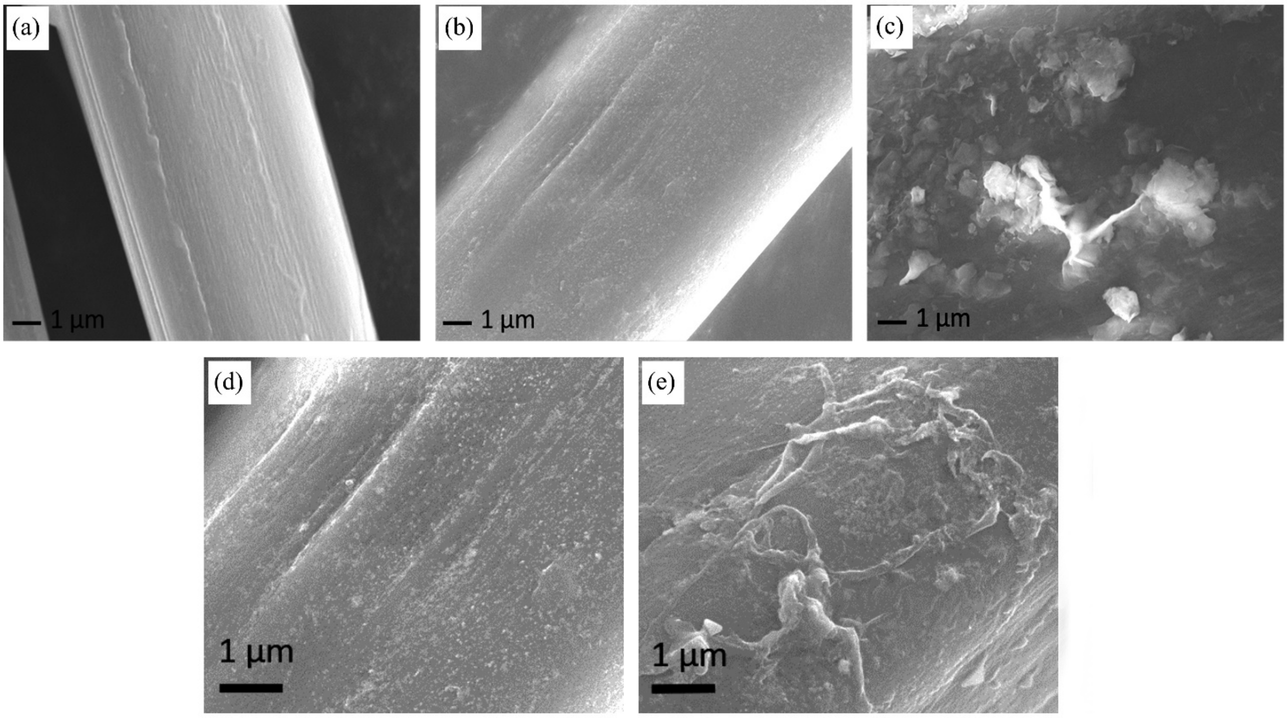

Figure 6 SEM photographs of (a) silk fabrics, (b) silk fabric dyed with AgNPs, (c) silk fabrics dyed with AgNPs treated MMT at a magnification of 8000x, (d) silk fabric dyed with AgNPs, and (e) silk fabrics dyed with AgNPs treated MMT.

3.2 Flame retardant and antibacterial properties

Figure 7 shows the photographs of samples that tested the flame retardant property using the vertical flammability test method. It can be observed the char length of silk fabric, silk fabric dyed with AgNPs, and AgNPs treated MMT, which were 8, 6, and 5 inches, respectively. The result indicates that MMT could effectively strengthen the char formation ability of silk fabric since the sample treated with MMT had the shortest char length, which was certified for the flame retardant property [20,21]. The flame retardancy of the fabrics enhanced with the introduction of MMT can be described as follow. When the fabric was burning, the silicate slices arranged on the surface of the finished fabrics resist the diffusion of small molecules derived from combustion products, then slow down the migration rate of outside oxygen and play the role of flame retardant [15].

The antibacterial activity of samples was determined using *S. aureus* was shown in Figure 8 and Table 2. It was demonstrated that both silk fabrics dyed with AgNPs and AgNPs treated MMT samples exhibited excellent antibacterial activity at 100% reduction for *S. aureus,* which is gram-positive bacteria after 24 h. It is commonly acknowledged that the AgNPs (smaller than 10 nm) can penetrate bacterial cell walls (alter the cell permeability), subsequently change the structure of the cell membrane and cause cell damage [26]. Generally, gram-negative bacteria are more susceptible to AgNPs since the cellular wall of gram-negative bacteria is narrower than that of gram-positive strains. The gram-positive bacteria with the thick cellular wall may reduce the penetration of nanoparticles into cells. It was suggested that the uptake of AgNPs is important on the antibacterial effect of AgNPs on gram-negative and gram-positive bacteria [27,28].

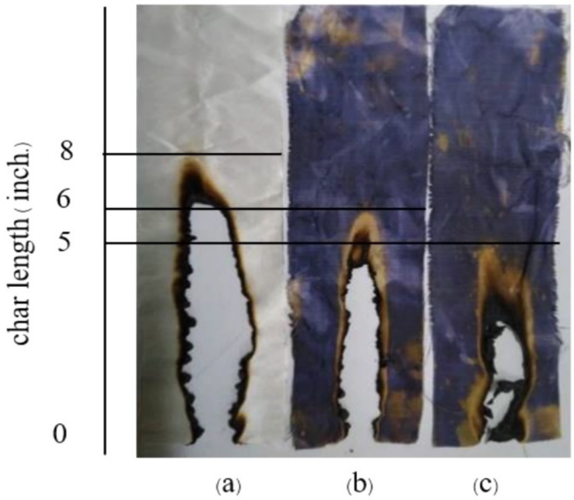

Figure 7 Flame-retardant of (a) silk fabrics, (b) silk fabrics dyed with AgNPs, and (c) silk fabrics dyed with AgNPs treated MMT.

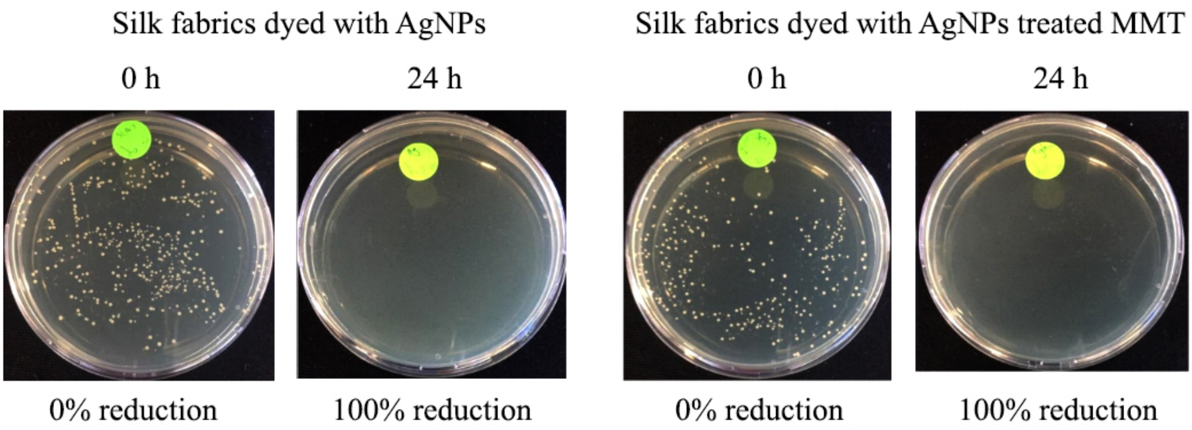

Figure 8 Numbers of bacteria *S.aureus* on silk fabrics dyed with AgNPs and Silk fabrics dyed with AgNPs treated MMT at 0 h and 24 h.

Table 2 Antimicrobial activity against *S.aureus* of silk fabrics dyed with AgNPs and Silk fabrics dyed with AgNPs treated MMT

Samples	*Staphylococcus aureus*					
	CFU/mL		%Reduction	Log CFU/mL		%Reduction
	0 h	24 h		0 h	24 h	
Silk fabrics dyed with AgNPs	$2.58\times10^6 \pm 9.29\times10^4$	0.00 ± 0.00	100	6.41 ± 0.02	0.00 ± 0.00	100
Silk fabrics dyed with AgNPs Treated MMT	$2.51\times10^6 \pm 1.10\times10^4$	0.00 ± 0.00	100	6.40 ± 0.02	0.00 ± 0.00	100

4. Conclusions

The color of prepared silver colloids after adjusting the pH value to 4 and 5 by adding dropwise acetic acid, was changed from blue to violet and dark blue, respectively. In this study, the effects of time and temperatures of the dyeing process were performed, and it was found that the optimum condition for complete dyeing silver colloids on silk fabric was at 100 °C for 90 min. It was observed by SEM that AgNPs and MMT were dispersed and covered on the surface of silk fabrics. Moreover, flame-retardant property of MMT could effectively strengthen the char formation ability of silk fabric and silk fabric dyed with AgNPs. The antibacterial test demonstrated the good antibacterial activity against *S. aureus* of silk fabrics dyed with AgNPs and AgNPs treated with MMT which were both 100% reduction.

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