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RESEARCH ARTICLE

Self-assembly silver nano particles monolayer on wool fabrics through polyelectrolyte complexation and study its finishing properties

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Abstract

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..... A stable silver nano particles (Ag NPs) colloidal solution was synthesized chemically via the reduction of silver nitrate using sodium borohydride as a reducing agent and sodium citrate as a stabilizer. Thus obtained Ag NPS were characterized by UV-vis spectra for the estimation of Ag NPS formation and TEM for determination of size and shape .These Ag NPs have been applied to the modified wool fabric by two polyelectrolytes, Poly (sodium -4-styrene, sulphonate (PSS) and Polyethylenimine (PEI) for particle monolayers deposition via colloid self-assembly. The modified wool fabrics treated with Ag NPs were evaluated by UV-vis spectra, SEM and EDX, tensile strength (TS) and contact angle measurement in addition to a bioassay of antibacterial activity. The dyeing behavior of the modified wool fabrics treated with Ag NPs and dyed with anionic and cationic dyes has been also studied as colorimetric data and fastness properties. The results indicate that the size of the stable Ag NPs in the colloidal solution was in range of 7.43-13.40 nm and the modified wool fabrics treated with Ag NPs before dyeing not only improve the TS, but also the antimicrobial efficiency of the fabric against B.subtilis, S.aureus and E.Coli. Further, the modified fabrics treated with Ag NPs and dyed with anionic dyes show very good colorimetric data and fastness properties. Moreover, the advanced wool fabrics treated with Ag NPs exhibit a great potential toward the functional properties of wool for textiles, health and medical application.

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INTRODUCTION

Nanotechnology brings together engineering, materials and equipment at the nano scale and it was important in various science and technology disciplines. Silver nanoparticles (Ag NPs) monolayers at solid substrates provides a wide range of practical applications for producing photonic and antireflective materials[1], as a catalysis of chemical reactions[1, 2], medicine [3, 4], biosensors [5, 6], biological probes and markers [7, 8]. Due to its excellent biostatic properties, they was also used to modify surfaces of various materials, in particular fibers or polymers [9, 10] which applied in consumer products such as clothes, laboratory and surgical gowns, and dressing bandages [10]. Currently, the high biological activity of Ag NPs, as well as a variety of other characteristics, is closely related to their size, shape and surface charge [11-13]. Previously, Ag NPs colloidal solution was prepared by different methods such as chemical methods [14], electrochemical methods, photochemical methods, sono chemical methods and other methods based on laser or radiolysis processes. However, these methods require special equipment, which makes them very expensive and also the purity and stability of Ag NPs monolayers is often not sufficient and non homogeneity [15]. Therefore, it is necessity to avoid these problems by using the colloid self-assembly methods of

Ag NPs from its stable suspensions and produced a homogeneous Ag NPs monolayers by adjusting the reaction parameters of this process and form diffusion controlled deposition. The most popular applied method to obtain nobel metal particles (e.g. Ag NPs), is the chemical reduction of silver salts by sodium borohydride on sodium citrate or other polymeric stabilizers [15, 16]. Compared to other methods, it's relatively simple and efficient and the potential applications of such homogenous monolayers produced by colloid self-assembly, were also reported in some literature [15-21]. In Ocwieja et al. [22] described a method of obtaining Ag NPs colloid solution from silver nitrate precursor, sodium borohydride and tri sodium citrate in which all reagents can play a dual role as a reducer and stabilizer in the nanoparticles synthesis methods in which combining of both reagents lead to obtain nanoparticles colloidal solution characterized by narrow size distributions and high stability which is important in the process of deposition of nanoparticles on the fabric [9, 23-25].

Polyelectrolyte complexes (PECs) have attracted a great interest of scientists to develop a wide range of applications such as nanofiltration [26], coating [27], tissue engineering [28, 29] and encapsulation [30]. PECs have been successfully developed on a numerous of different substrates e.g glass, quartz, mica, silicon, gold, silver [31] and also textile fabrics [32, 33]. Polyelectrolyte are often used to modify the textile surfaces to textile materials containing desirable functional groups on their surfaces associated with specific and new properties [34, 35]. The polyelectrolyte layers are very stable and not removed by mechanical stress.

On the other hand, deposition of Ag NPs on wool fabric provides many new and improved its properties [36-37]. Ag NPs loaded wool fabric could be used in medical and textile applications such as health care, sock, wound dressing, protective suits, personal care product, comfort, clothing and others [38].

In this study, Ag NPs have been synthesized by chemical methods. The stable Ag NPs colloidal solution has been prepared by the reduction of silver nitrate salt using sodium borohydride as a reducing agent and trisodium citrate as a stabilizer agent. Therefore, our strategy is based on coating wool fabrics with polyelectrolyte supporting layers from polystyrene sulphonate (PSS) and polyethyleneimine (PEI) to provide the fabric surface with a plenty of cationic charge groups, to obtain a uniform monolayers distribution of Ag NPs which diffused well and embedded to form a complex between wool fabrics and Ag NPs . Also, the effect of different concentration of crosslinking agent PSS (0, 20 &1000 ppm) on the deposition of Ag NPs monolayer on wool fabric was studied. Additionally ,the existence of Ag NPS in the colloidal solution was confirmed by UV-vis,TEM and partical size distribution .Whereas , the modified wool fabric with polyelectrolyte layer by layer PSS and PEI coated by Ag NPs monolayers produced by colloid self – assembly was characterized by UV-vis , SEM and EDX ,TS , elongation %, contact angle and an antibacterial activity .The colorimetric analysis of the modified wool fabric treated with Ag NPs before and after dyeing with anionic and cationic dyes and its fastness properties were also evaluated in this study.

2. Experimental

2.1. Materials

Pure Wool woven fabric (300 g/m²), supplied by Misr Company for Spinning and Weaving, Mehalla El-Kubra-Egypt. The fabric was soaped with 2 g/l of non-ionic detergent (Hostapal CV; Clariant, Egypt) at 60°C for 30 min, then washed thoroughly with rinsed water and air-dried at room temperature. The chemicals employed in this study were: Silver nitrate extra pure was purchased from Mumbai-India, sodium borohydride, trisodium citrate, Polyelectrolytes: Poly sodium-4-styrene sulfonate (PSS having Mwt.of 70.000) and polyethyleneimine solution (PEI having Mwt. of 60.000) were obtained from Sigma-Aldrich - Germany. All other chemical reagents were of a laboratory grade reagents. The dyes used in this work were: C.I. Reactive Blue 19 (RB19), C.I. Direct Red 79 (DR79) and C.I. Basic Red 24 (BR24). The dyes were kindly supplied by Ciba (Egypt).

2.2. Methods

2.2.1. Preparation of silver Nanoparticles (AgNPs)

AgNPs suspension was prepared by chemical reduction method of silver nitrate [22, 36] by dissolving 16 mg sodium borohydride and 147 mg trisodium citrate into 100 ml of distilled water. Then, while stirring with homogenizer for 15 min, 50 ml of 1mM AgNo₃ solution was added drop by drop with vigorous stirring into the reduction mixture for another 15 min turning the solution to yellow color indicating the reduction of Ag⁺ ion and then stirring was continued at room temperature for further 1 hr.

2.2.2. Treatment of wool fabric with polyelectrolyte and AgNPs

0.5g of wool fabric was first immersed into different concentration of PSS (0- 20 and 1000 ppm) aqueous solution at pH=4, for 30 min at room temperature following by washing thoroughly the treated fabric with rinsed water. Secondly, the PSS treated fabric was immersed into 1000 ppm of PEI aqueous solution at pH=4 for 30 min at room

temperature. Finally, the wool fabric covered with both PSS and PEI monolayers were rinsed well with water and immersed in 50 ml of the AgNPs suspension at pH=5.5 with good shaking for 30 min.

2.2.3. Dyeing methods

The untreated and AgNPs treated wool fabrics were introduced into a dyebath of 2% (owf) shade, liquor ratio 40:1 at pH 4.5 using I.R. dyeing machine and the temperature was raised to the desired temperature (100°C) gradually over 20 min, and then the dyeing process was continued at this temperature for 60 min. Then, the dyed fabrics were removed from the dye pot, rinsed in cold water and washed with 2 g/l non ionic detergent at a liquor ratio of 50:1 at 60 °C for 30 min and finally rinsed with water and air-dried [36].

2.3. Measurements

2.3.1. Characterization of Ag NPs suspension

Uv-vis spectra have been used as a sensitive technique to prove the formation of AgNPs as it exhibits an intence absorption peak due to the surface Plasmon resonance. Thus, AgNPs formed in suspension were recorded by Shimadzu UV-2401PC UV/visible spectrophotometer at the λ_{max} 200 to 700 nm. The diameter and size distribution were obtained by transmission electron microscope (TEM) JEOL-JEM-1200. The measurements were prepared by placing two drops of the colloid solution on 400 mesh copper grid coated by an amorphous carbon film and the remaining solvent was evaporated at room temperature. The particle size and size distribution histogram was determined by the particle size analyzer Malvern Instruments Ltd.

2.3.2. Characterization of wool fabrics treated with Ag NPs

Uv-vis spectra of untreated and treated wool fabrics with Ag NPs were measured using spectrophotometer (Hunter Lab Ultra Scan PRO Spectrophotometer (USA)) interfaced with a personal computer from wavelength range of 300-800 nm. **Scanning electron microscope (SEM)** was used to study the morphology of the surface of the untreated and treated wool fabrics with Ag NPs Model Philips XL 30 with an EDX unit attached, with accelerating voltage of 30 kV and magnification between 10.000 x and 400.000 x; all the wool samples were coated with gold before SEM testing. **EDX analysis** was also studied to identify silver on the wool fabric surface and the weight percentages of oxygen, nitrogen and silver. In addition, **the warp tensile strength** was determined for untreated and treated wool fabrics with Ag NPs was measured with deionized water contact angle measurements using compact video microscope manufactured by SDL-UK. Deionized water was automatically dropped onto the fabric surface according to ASTM D724-99 standard test method for surface wettability of paper and ASTM D5946-96 standard test method for corona-treated polymer film.

The antibacterial activity of silver treated wool fabrics was tested against Bacillus subtilis NRRL 543, Staphylococcus aureus NRRL B-313 (Gram-positive bacteria), Escherichia coli NRRL B-210 (Gram-negative bacteria) using nutrient agar medium and the antifungal activity was tested against Candida albicans NRRL Y-477 using Sabouraud dextrose agar medium in sterile Petri dishes. All tested microorganism were obtained from Northern Utilization Research and Development Division, U.S. Department of Agricultural Peoria, Illinois, USA. Silver coated wool fabric and blank fabric samples were assayed by the agar diffusion method [40]. Fabric specimens were placed in intimate contact with nutrient agar, which has been previously seeded with inoculums of each test organism. After incubation for 24 h in an incubator at 30°C, the plates were visually examined for zones of inhibition around and on the silver treated wool fabrics samples. The size of the inhibition zone was measured at two cross sectional point and the average was taken. All experiments were performed in triplicate. The antibacterial effect was also determined by the standard method AATCC-100 with all tested strains by the agar plate method, and the duration of microbial growth was 24 hours after which, colonies were counted and bacteria reduction was calculated from this equation:

R(%)=(C-A/C)×100

Where R is the bacterial reduction ratio, A is the number of bacterial colonies from the untreated fabrics and C is the number of the bacterial colonies from the treated fabrics.

2.3.3. The Color measurements

The spectrophotometeric colorimetric data of the untreated and treated wool fabrics with AgNPs before and after dyeing was examined using Hunter Lab Ultra Scan PRO Spectrophotometer, USA. The colorimetric data derived from CIE LAB color space data was expressed as L^* , a^* , b^* measurements which describe the hue of the color, where L^* is the lightness from black (0) to white (100), a^* is a red (+)/green (-) ratio and b^* is yellow (+)/blue (-) ratio. In order to achieve correct readings, three readings per sample were averaged.

2.3.4. Fastness properties

Fastness testing for the untreated and treated wool fabrics with AgNPs before and after dyeing was carried out according to ISO standard methods. The specific tests were: ISO 105-X12 (1987), color fastness to rubbing; ISO 105-C02 (1989), colour fastness to washing; and ISO 105-E04 (1989), color fastness to perspiration.

3. Results and discussion

The target of loading Ag NPs is very importance in textile industry and generates nowadays a very active scientific and technological field. Such as developed polyelectrolyte techniques e.g. PSS/PEI in which PSS act as a cross linking agent associated with embedded Ag NPs on its layers to form a complex between polymer and Ag NPs to generate numerous applications. Previously, different techniques has been used to functionalized wool fabric surface using nano particles suspension preparation followed by loading on the modified fabrics or synthesis and in-situ incorporation of Ag NPs into the fabric [36, 37, 41-44]. Our research deals with functionalized wool fabric surface by a precursor PSS with different concentration (0, 20& 1000) as a cross linking agent to let the wool fabric modified by positively charge PEI as a simple method by the particle deposition mechanisms to obtain uniform monolayers coverage of AgNPs which diffused well and embedded to form a complex between wool and Ag NPs [22, 45]. The first step focused on synthesizes silver nano particles self-assembly which is confirmed by UV-vis and TEM, then deposit it on the modified wool fabrics from the aqueous suspension associated with uniform distribution. Also, followed by the application of Ag NPs complex as antibacterial activities and improving the physical properties of the treated wool fabric. Second step, focused on the characterization of this treated wool fabric, Ag NPs monolayer coverage by UV-vis, SEM and EDX, TS and contact angle measurement in addition to a bioassay of antibacterial activity. Third step focused on enhancing the dyeability of wool fabrics using anionic and cationic dyes and improving their fastness properties. The mechanism of the reaction can be expressed as follows:

$$AgNO_{3} + NaBH_{4} + C_{6}H_{5}O_{7}Na_{3} + 2H_{2}O \rightarrow Ag + 1/2H_{2} + 1/2 B_{2}H_{6} + C_{6}H_{5}O_{7}H_{3} + H + O_{2} \uparrow + NaNO_{3} + 3 Na$$



3.1. Characterization of Ag NPs suspension

3.1.1. UV-vis spectra

UV-vis absorbance spectra of freshly prepared Ag NPs suspension and after storing for 1 week to evaluate the stability of the suspension was shown in Fig.1.

The freshly prepared Ag NPs suspension exhibited intense yellow color due to plasmon resonance of the nano particles which was confirmed by exhibiting a sharp maximum absorbance peak at wavelength 389 nm associated with no shoulder at higher wavelengths as shown in Fig.1a. This observation indicates that, relatively small particles of Ag were obtained[41, 42] and the suspension was fairly mono dispersed and there is no larger aggregates [43]. However, after storing the freshly prepared Ag NPs suspension for 1 week, the absorbance spectra showed a red shift at the wavelength around ~ 425 nm with exhibiting intense brown color, associated with decreasing the absorbance value from 1.20 to 0.85 and the absorbance peak become broad .This result, may be due to the

aggregation of Ag NPs with time (1week). Both spectra exhibit plasmon absorption band at \sim 400nm which is the characteristic band of Ag NPs.



Fig.1. UV-vis spectrum of Ag NPs suspension. a) – Freshly prepared and b) – Stored for one week Reaction condition: 16 mg/100 ml sodium borohydride, 147mg/100 ml trisodium citrate and 1mM/50 ml of Ag NO₃, stirred well at room temperature for 1 hour.

3.2.2. Transmission electron microscopy TEM

Fig.2. shows the TEM images of freshly prepared Ag NPs suspension and after storing it for 1 week. From Fig.2 (a & b) it can be seen that, Ag particles exhibit spherical shapes with diameter ranging from 7.43 nm to 13.40 nm and are quite monodispersed with enough amount and homogenous (not aggregated). However, Fig.2 (c) clarifies that the TEM images of Ag NPs particles of the suspension stored for 1 week shows spherical shape and not homogenous (aggregated). This result may be attributed to the formation of several Ag NPs that form silver ions as the time of storage increased from 0-1 week, which verifies aggregation and let the dispersion of Ag NPs not homogeneity.

The particle size and size distribution of the prepared Ag NPs suspension were analyzed in detail as shown in Fig.3. It was illustrated form Fig.3a that the appearance of one peak in the histogram indicates that the resultant suspension contains a well stabilized Ag NPs solution (100%) associated with a diameter of 7.828 nm. Also, from fig.3b it was found that, the average particle size was 7.828 nm with the standard deviation of 5nm (relative standard deviation 0.31).



Fig.2. TEM image of Ag NPs suspension. (a&b) - Freshly prepared suspension, c) Stored the suspension for one week

Reaction condition: 16 mg/100 ml sodium borohydride, 147 mg/100 ml trisodium citrate and 1mM/50 ml of Ag NO₃, stirred well at room temperature for 1 hour.



Fig.3. Particle size distribution of Ag NPs. a) Size distribution by intensity and b) - Statistical graph by intensity

Reaction condition: freshly prepared Ag NPs suspension (16 mg/100 ml sodium borohydride, 147mg/100 ml trisodium citrate and 1mM/50 ml of Ag NO₃, stirred well at room temperature for 1 hour).

3.2. Characterization of wool fabric treated with Ag NPs

3.2.1. UV-vis spectra

The Uv-vis absorbance spectra of the untreated and treated wool fabrics with Ag NPs which was modified with different concentrations of PSS (0, 20 &1000 ppm) and 1000 ppm PEI by the polyelectrolyte layers was evaluated as shown in Fig.4. The figure shows that the untreated and treated wool fabrics with Ag NPs were not shown any absorption band. This result may be attributed to that the untreated and treated wool fabrics a, b, c and d have no obvious plasmon absorption band of Ag NPs at the end of reaction [37]. However, increasing the concentration of PSS from (0-1000 ppm) lead to increasing the absorbance spectrum compared to the untreated fabric which was associated with darker brownish color, as the density of the Ag NPs particle deposition on the surface of modified wool fabrics increased.



Fig.4. UV-vis absorbance spectra of the untreated and treated wool fabrics modified with different concentration of PSS, 1000 ppm PET and AgNPs. a)- Untreated fabric (Blank), b)- Blank fabric treated with Ag NPs (zero PSS), c)- Wool fabric treated with 20 ppm PSS, 1000ppm PEI & AgNPs and d)- Wool fabric treated with 1000 ppm PSS, 1000 ppm PEI & AgNPs.

3.2.2 Scanning electron microscope (SEM) and EDX

The morphology and dispersion of Ag NPs deposited on the unmodified and modified wool fabric surface was illustrated in Fig.5. The image of both untreated wool (Fig.5a) and treated wool with Ag NPs (Fig.5b) shows the distinct scales and the overlapping between them on the wool surface. Also, the images of the modified wool fabrics with 20 ppm PPS and 1000 ppm PEI treated with Ag NPs were shown in Fig.5c. The image indicates that, the surface of fibers is covered by a thin layer of Ag NPs associated with uneven distribution on the surface. This result may be due to decreasing the +ve charge density on the wool surface which decrease the interaction between PEI and Ag NPs. However, increasing the concentration of PSS to 1000 ppm will increase the electrostatic interaction of -ve charges sulphonate groups and imine groups of PEI and there were excess positive charges on the surface. Although, the surface of wool fabrics was covered by a sufficient layer from Ag NPs which had a wide range of distribution and the scales were not clear i.e. the surface was completely coated with Ag NPs as shown in Fig.5d.





Fig.5. SEM image of untreated and treated wool fabrics with Ag NPs using different concentration of PSS. a)-Untreated (Blank), b)- Treated Blank fabric with Ag NPs, c)- Treated wool fabric with 20 ppm PSS, 1000 PEI and Ag NPs, d)- Treated wool fabric with 1000 ppm PSS, 1000 ppm PEI and Ag NPs.

Chemical composition of treated wool fabric was checked by EDX analysis. Fig.6 (a, b &c) show the spectra of modified wool fabrics with different concentration of PSS (0, 20, & 1000 ppm) associated with 1000 ppm PEI and Ag NPs respectively. The peak appeared at 3-4 Kev in each concentration attributed to the presence of silver. On the other hand, loading of sufficient amount of Ag NPs on wool fabric was confirmed by EDX pattern which indicated that Ag NPs show good incorporation into wool fabric surface.



Lsec: 30.0 0 Cnts 0.000 keV Det: Octane Pro Det Reso



Fig.6. EDX of wool fabric treated with Ag NPs in the presence of different concentration of PSS. a)- Treated Blank fabric with Ag NPs, b)- Treated wool fabric with 20 ppm PSS, 1000 PEI and Ag NPs, c)- Treated wool fabric with 1000 ppm PSS, 1000 ppm PEI and Ag NPs.

3.2.3. Physical and mechanical properties of Ag NPs treated wool fabrics

Table 1 shows the mechanical properties of untreated and treated wool fabrics with Ag NPs. It was obvious from the table that, there is a decrease in the tensile strength (TS) according the following order: untreated wool fabrics (A) > untreated wool fabrics treated with Ag NPs (B) > modified wool fabric treated with 20 ppm PSS, 1000 ppm PEI and Ag NPs (C) > modified wool fabric treated with 1000 ppm, 1000 ppm PEI and Ag NPs(D), but not very significant. On the other hand, the TS of wool fabric continue to decrease as the concentration of PSS increases from 0 – 1000 ppm. Moreover, the elongation at break of treated wool fabric with Ag NPs was higher than the untreated fabric due to the higher frictional force of fibers. Breaking of the chains as the concentration of PSS increases from 0 – 1000 ppm show a higher tensile strain. This result may be attributed to the smaller size of Ag NPs, which enter in between the modified wool fabric and act as filler or crosslinking agent which also contribute to load sharing phenomenon during load application [36].

The contact angle measurements were performed on untreated and treated wool fabrics with Ag NPs (A, B, C & D) in order to evaluate the hydrophilicity and / or hydrophobicity of wool fabrics as shown in the Table1. It can be seen from Table 1 that the contact angles of the blank wool treated with Ag NPs (B) and treated with 20 ppm PSS, 1000 ppm PEI and Ag NPs (C) were similar to the blank fabric (A) and obviously lower than that treated with 1000 ppm PSS, 1000 ppm PEI and Ag NPs (D). This result may be attributed to that, as the concentration of PSS increased from 0-1000 ppm, the positive charge density on the wool fabric surface will be increased and the chemical reaction between PEI and Ag NPs will also be increased and change the surface to be more hydrophobic.

| Fabric samples | Tensile strength (kgf) | Tensile strain (%) Contact ang (°C) 26.50 138.00 27.50 136.50 | | | | |
|----------------|------------------------|---|--------|--|--|--|
| Α | 67.820 | 26.50 | 138.00 | | | |
| В | 64.344 | 27.50 | 136.50 | | | |
| С | 65.122 | 28.33 | 136.50 | | | |
| D | 63.788 | 29.68 | 150.00 | | | |

| Table 1: | | | | | | | | |
|-------------------|---------------|-------------|-----------|-------|-----------|---------|---------|-------|
| Mechanical | properties of | untreated a | nd silver | nanop | articales | treated | wool fa | brics |

A: Blank fabric (untreated)

B: Blank fabric treated by Ag NPs

C: Blank fabric treated by 20 ppm PSS, 1000 ppm PEI & Ag NPs

D: Blank fabric treated by 1000 ppm PSS, 1000 ppm PEI & Ag NPs

3.2.4. Antimicrobial studies

Antibacterial activity of silver nano particles coated wool fabric was determined in terms of inhibition zone formed on agar medium and reduction percent. The Ag NPs have been demonstrated to exhibit wide range of activity against bacteria and viruses [44]. The effect of different concentration of PSS on the antibacterial activity of untreated and treated wool fabrics against different microorganisms before and after washing was shown in Table 2 and Fig.7. It is clear from the table that the untreated wool fabric (sample A) did not show any antibacterial properties. However, antibacterial efficient or property of Ag NPs treated fabrics is better and show an improvement than that of the untreated fabric especially, after increasing the concentration of PSS from 0 - 1000 ppm. This result may be due to increasing the positive charge density of imines groups of PEI on the wool fabric surface which increased the chance of the chemical reaction between PEI and Ag NPs, which can interact with the cell wall of bacteria through the physical and ionic phenomenon [45,46] and hinder the growth of the microorganisms and increased the inhibition zone as well as the reduction percent and exhibited good bacterial activity before and after washing due to the silver release to the environment [47]. In contrast, after washing the treated wool fabrics with Ag NPs several times from 0, 5 & 10 wash cycles the effectiveness of these samples against different microorganisms as bacteria reduction percentage will be significant decreased as the washing cycles increased. This result depends on the amount of Ag NPs on wool fabric and also on the state of their distribution i.e. this phenomenon is associated with weak bonding between AgNPs and wool surface [45]. Also, the results indicated that antibacterial activity of sample C & D as a percent reduction of bacteria shows 95% and 96% antibacterial reduction against B.subtilis, 94% and 96% against S.aureus and 93% and 94% against E.Coli, 92% and 93% against C. albicans respectively was more effective than sample A & B. These results may be due to that C. albicans funji are more resistance to AgNPs than Gram positive and Gram negative bacteria and confirmed that AgNPs have better antibacterial behavior against Gram positive and Gram negative bacteria on wool fabric of sample C & D . Furthermore, Fig.7 shows that sample A & B have no zone of inhibition. Although, sample C & D exhibited efficient antibacterial activity and produce inhibition zone of 26, 25, 25 and 23 mm against B.subtilis, S.aureus, E.Coli and C. albicans respectively in sample C. While, sample D show inhibition zone of 27, 26, 26 and 24 mm against B.subtilis, S.aureus, E.Coli and C. albicans respectively. The good antibacterial activity after 10 cycles of washing for samples C and D proved approximately strong durability of AgNPs treated wool fabric may be due to the presence of the polyelectrolyte layers which lead to strong chemical interaction of Ag NPs to the fabric. In general, it is attributed that bacterial inhibition of Ag NPs may be due to their large surface area which leads to better contact with micro-organisms through bond formation on the surface and provide higher free mobility and improve disinfecting effect by interacting closely with bacteria membranes and damage it which disrupts biochemical processes leading to bacterial death.

| | | Reduction of bacteria (%) | | | | | | | | | |
|------------------|----------------|---------------------------|------------|-------------------|-------------|--|--|--|--|--|--|
| Fabric sample | Washing cycles | Gram +v | e bacteria | Gram -ve bacteria | Fungi | | | | | | |
| | (100) | B. sulitilis S. aureus | | E.Coli | C. albicans | | | | | | |
| | 0 | - | - | - | - | | | | | | |
| Α | 5 | - | - | - | - | | | | | | |
| | 10 | - | - | - | - | | | | | | |
| | 0 | - | - | - | - | | | | | | |
| В | 5 | - | - | - | - | | | | | | |
| | 10 | - | - | - | - | | | | | | |
| | 0 | 95 | 94 | 93 | 92 | | | | | | |
| С | 5 | 87 | 85 | 88 | 83 | | | | | | |
| | 10 | 76 | 75 | 74 | 30 | | | | | | |
| D | 0 | 96 | 96 | 94 | 95 | | | | | | |
| | 5 | 87 | 86 | 89 | 84 | | | | | | |
| | 10 | 79 | 77 | 75 | 40 | | | | | | |

| Table 2: | |
|--|---|
| Effect of PSS concentration on the antibacterial | properties of treated wool fabric with Ag NPs |

The Key of A, B, C& D see Table 1



Fig. 7: Antibacterial activity versus repeated washing cycles of wool fabrics (B, C & D) treated with Ag NPs. B: Blank fabric treated by Ag NPs

C: Blank fabric treated by 20 ppm PSS, 1000 ppm PEI & Ag NPs

D: Blank fabric treated by 1000 ppm PSS, 1000 ppm PEI & Ag NPs

3.3. Colorimetric data for untreated and treated wool fabric before and after dyeing

To investigate the color properties of the untreated and treated wool fabrics with Ag NPs, the colorimetric data was measured for them before and after dveing using three selected anionic and cationic dves, namely C.I. RB19, C.I. DR 79 and C.I. BR 24 respectively. This colorimetric data were measured for both untreated and treated wool fabric to study the effect of Ag NPs on the color of dyeing wool fabrics with these dyes and are reported in Table 1. It was observed that Ag NPs treatment of wool fabrics caused a color difference on the direction L*(lightness/darkness values from 100-0 representing white to black), a* (run from negative i.e. green to positive i.e. red) and b* values (run from negative i.e. blue to positive i.e. vellow). Also, Table 1 indicate that the color of untreated wool fabric A (Blank) is creamy with a high L* value and zero a* values and 9 b* values. In contrast, with the blank fabrics, all the modified wool fabrics with different concentration of PSS (0-1000 ppm), 1000 ppm PEI and Ag NPs have significantly lower L* value before dying process, as the lightness of wool reduced from 82.01 to 46.25 as the concentration PSS increased and due to that the density of Ag NPs on the fabric surface increase and also the color become dark reddish brown. Also, a* values were increased from -0.42 for untreated sample A to 4.76 for wool treated with Ag NPs as the PSS concentration increased (sample B, C and D). Whereas, the b* values were 9.00 for sample A and it was increased as the concentration of PSS increased which increasing the Ag NPs from 11.54 to 19.74 for the treated fabrics associated with dark yellowness brown color before dying process. However, after dyeing the untreated and treated wool fabric with C.I. RB19 lightness (L*) is decreased from 25.62 for the untreated fabric A to 22.09 for the treated fabrics from sample B, C and D. This result may be due to the coloration of fabric with the blue dye after treatment with Ag NPs, which become more deep bluish by using a higher concentration of PSS which lead to a more deposition of Ag NPs on the surface of PEI. The decrements in a* values following the order A>B>C<D for the untreated and treated wool fabric with Ag NPs signing to some interference of redness color to the blue color of the dyed fabric showing a bathocromic shift of the wave length from 600 for the untreated dyed fabric A to 615 nm for the treated fabric with Ag NPs and dyed with C.I. RB19 and the hue change to bluish red. The negative charge of b* values indicate that, the color of the treated fabric was exactly range from blue to dark blue color following the order A < B < C < D. Moreover, in case of dyeing the untreated and treated fabric with C.I. BR 24 it was found that L* gradually increased from 30.44 for the untreated dyed fabric A to 40.44 for the treated dyed fabric ('B, C and D) with 0, 20&1000 ppm PSS respectively and 1000 ppm PEI and Ag NPs. This result of increment may be attributed to the coloration of fibers, which become more lightly by using a high concentration of PSS which lead to more concentration of Ag NPs on the surface and the color change. Although, the decrement in a* values was associated with lighting the redness color of the treated and dyed wool fabric with Ag NPs. While, the significant decreasing in b* values from 4.62 for untreated dyed fabric A to 1.56 for the treated dyed wool fabrics C is attributed to the yellow color interference with the red color of the dye after dyeing process. Furthermore, in case of dyeing the untreated and treated wool fabric with C.I. DR 79 it was observed that L* decreased gradually from 24.70 for untreated 'A to 22.17 for the treated fiber with Ag NPs as a result for more deeply color by using high concentration of PSS and Ag NPs. The red/green ratio (a*) values are recorded to be 37.35, 36.17, 28.70 and 28.33 for the samples A, B, C and D respectively. The decrement in a* values according to increasing some of the redness color more for samples C and D. The yellow/ blue ratio (b*) value decreased from 12.90 for the untreated A and B samples to be in range of 9.35-9.31 i.e. fixed for the treated fabrics C and D. This may be due to the yellow color acquired after treatment. In general it was emphasis that: 1)- the results of colorimetric data of the treated wool fabrics are agree with UV-Vis spectrophotometric data of the absorbance spectrum of anionic and cationic dye. Both anionic dyes (C.I. R B19 and C.I. DR 79) caused bathochromic shift of wave length (600-645 nm) and (525-540 nm) respectively, while C.I. BR 24 show the same wave length. 2) - The darker color of treated and dyed wool fabrics using C.I. R B19 and C.I. DR 79 was achieved by increasing the concentration of PSS from 0-1000 ppm and 1000 ppm PEI which lead to increase the positive charge density on the surface of fabric and due to that the concentration or deposition of AgNPs on the surface also increased. 3) - The treated and dyed wool fabrics using C.I. R B19 and C.I. DR 79 show blue and red color with different shades from blue to dark blue in case of C.I. R B19. Also in case of C.I. DR 79 the color changes from red to dark scarlet red [48]. This result indicates that the nature of color was not changes as the concentration of PSS increased from 0-1000 ppm. However, treated and dyed wool fabric with C.I. BR 24 show change in the hue of the color. This result is attributed to the types, molecular weight and structure of the dye used.

| Table 3: | |
|--|-----|
| Colorimetric data of untreated and treated wool fabrics with Ag NPs before and after dyeing with anionic and cationic dy | yes |

| Fabric | В | efore dyein | Ig | Fabric | After dyeing | | | | | | | | |
|--------|-------|-------------|------------|------------|--------------|-----------|--------|-------|-----------|------|-------|-------|-------|
| sample | | sample | C.I. RB 19 | | | C.I.BR 24 | | | C.I.DR 79 | | | | |
| | L* | a* | b* | | L* | a* | b* | L* | a* | b* | L* | a* | b* |
| Α | 82.01 | -0.42 | 9.00 | ∕A | 25.62 | 5.12 | -33.82 | 30.44 | 33.79 | 4.62 | 24.70 | 37.35 | 12.90 |
| В | 74.99 | 1.28 | 11.54 | ′B | 26.01 | 3.62 | -31.21 | 34.97 | 33.54 | 1.68 | 24.22 | 36.17 | 12.19 |
| С | 44.79 | 5.89 | 18.87 | ′ C | 24.48 | 1.51 | -21.79 | 31.18 | 26.01 | 1.56 | 22.17 | 28.70 | 9.35 |
| D | 46.25 | 4.76 | 19.74 | D | 22.09 | 2.65 | -26.80 | 40.44 | 23.37 | 2.00 | 22.30 | 28.33 | 9.31 |

A: Blank fabric (untreated)

B: Blank fabric treated by Ag NPs

C: Blank fabric treated by 20 ppm PSS, 1000 ppm PEI & Ag NPs D: Blank fabric treated by 1000 ppm PSS, 1000 ppm PEI & Ag NPs

3.4. Fastness properties

As shown in Table 4, the fastness tests of washing, light, crocking and perspiration of the untreated and treated fabrics with AgNPs that had been dyed with the anionic dyes C.I. RB 19 and C.I. DR 79 are very good towards perspiration and washing fastness. This result indicating the existence of strong bonds between the anionic dye molecules and the fabrics treated with AgNPs (ionic and covalent bonds for reactive dye and ionic bonds for direct dye. It was obvious that AgNPs on the fabric surface in fact act as a chelating agent (mordant) which increased the dye affinity towards the fabrics and improved its fastness by electrostatic interaction. Although, the resulting crocking fastness for treated wool with AgNPs was lower than the untreated fabrics and the dry- crocking fastness was relatively higher than wet crocking fastness. However, in case of dyeing the treated wool fabrics with cationic dye (C.I. BR 24) show poor fastness properties towards crocking, perspiration, washing and light than the untreated fabrics. Generally, the treated wool fabric with AgNPs not only improved the color strength but also improved the color fastness of the anionic dyes especially the direct dye which cause a major drawback [48].

4. Conclusion

The present work focused on the preparation of stable AgNPs suspensions which is appropriate for self assembly on wool fabric surface via polyelectrolyte complexation. The formation of AgNPs was confirmed by UV-visible absorption spectra which showed a characteristics band of AgNPs at 389 nm and TEM analysis which showed that the AgNPs were in spherical shape and their size was in range of 7.43-13.40 nm. Moreover, the existence of AgNPs uniform distribution monolayer on the modified wool fabrics was confirmed by UV-vis, SEM and EDX. Also, lower tensile strength and higher elongation percent may be due to introducing Ag NPs monolayers to the modified wool fabric. On the other hand, our results proved that as the concentration of PSS increased from 0, 20 to 1000 ppm, a uniform monolayers distribution of AgNPs with good regulation was produced. The antibacterial behavior of modified wool fabric and treated with AgNPs was determined against gram positive, gram negative bacteria and fungi through disc diffusion and quantitative method. However, modified and treated wool fabric with AgNPs shows good and higher antibacterial activity against gram positive, gram negative bacteria than fungi. Further, the durability of treated fabric after 5 washing is fair due to the chemical interaction between fabric and nanoparticles. It is also observed that there is considerable AgNPs on the treated wool fabrics was successfully enhances the colorimetric data of reactive and direct dyes and also improve the fastness properties towards washing and light fastness than the untreated wool fabric especially direct dyes which was the major drawback of most textile dyeing industry. The advanced of this wool fabric treated with polyelectrolyte and AgNPs monolayers may exhibit great potential for textiles and medical applications. Further studies will be done to improve the antibacterial laundering process for several times.

Abbreviation

| Silver nano particles | Ag NPs |
|--------------------------------------|--------|
| Ultraviolet-visible | UV-vis |
| Transmission electron microscope | TEM |
| Poly (sodium -4-styrene, sulphonate) | PSS |
| Polyethylenimine | PEI |
| Scanning electron microscopy | SEM |
| Tensile strength | TS |
| Polyelectrolyte complexes | PECs |

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| | | | | - | | | Fastness] | properties | | - | | | | | | | |
|---------------|----------------|------|------|--------------|------|-----|------------|------------|-----|-----|---------|-----|-------|--|--|--|--|
| Dvestuff | Samples | croc | king | Perspiration | | | | | | | Washing | | | | | | |
| Dyestuii | Sumples | drv | wet | | Acid | *** | | Alkali | *** | Α | С | w | Light | | | | |
| | | , | | A | C | W | Α | C | W | | | | | | | | |
| oric | Α | 4 | 3-4 | 4-5 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | | | | |
| l fal | В | 4 | 3-4 | 4-5 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 3-4 | | | | |
| dyed | С | 3 | 2 | 4-5 | 4 | 4-5 | 4 | 4 | 4-5 | 4 | 4 | 4-5 | 4-5 | | | | |
| Un | D | 3 | 2 | 4-5 | 4 | 4-5 | 4 | 4 | 4-5 | 4 | 4 | 4-5 | 4 | | | | |
| • | A | 4 | 3 | 4-5 | 4-5 | 4-5 | 4-5 | 4 | 4 | 4 | 4 | 4 | 4 | | | | |
| (B 19 | ∕ B | 4 | 3-4 | 4-5 | 4-5 | 4-5 | 4-5 | 4-5 | 4 | 4 | 4 | 4 | 4-5 | | | | |
| .г. в | ′C | 2-3 | 1-2 | 4-5 | 4-5 | 4-5 | 4-5 | 4 | 4-5 | 4 | 4 | 4 | 4-5 | | | | |
| 0 | ∕́ D | 3 | 1-2 | 4-5 | 4 | 4 | 4-5 | 3-4 | 3-4 | 4 | 4 | 4 | 4-5 | | | | |
| 4 | ^ A | 3-4 | 2 | 3-4 | 1-2 | 1-2 | 3 | 1-2 | 1-2 | 3 | 1-2 | 1-2 | 2 | | | | |
| iR 2, | ′B | 3-4 | 2 | 3-4 | 2-3 | 1-2 | 3-4 | 1-2 | 2 | 3 | 2-3 | 2 | 2 | | | | |
| . I. B | ′C | 2 | 1-2 | 3-4 | 3 | 2-3 | 3 | 1-2 | 1-2 | 3 | 3 | 2 | 2 | | | | |
| 0 | ∕∕D | 3 | 1-2 | 3-4 | 2 | 3 | 3-4 | 2-3 | 2-3 | 3-4 | 3-4 | 3 | 2-3 | | | | |
| _ | 'A | 3-4 | 3 | 4 | 4 | 4 | 4-5 | 4 | 4-5 | 4 | 3-4 | 4 | 5 | | | | |
| R 79 | ′B | 3-4 | 3 | 4 | 4 | 4 | 4-5 | 4 | 4-5 | 4 | 3 | 4 | 5-6 | | | | |
| C.I. D] | [/] C | 2 | 1-2 | 4 | 4 | 4 | 4-5 | 4 | 4-5 | 4 | 3-4 | 4 | 5-6 | | | | |
| - | D | 2 | 1-2 | 4 | 4 | 4-5 | 4 | 3-4 | 4-5 | 4 | 3-4 | 4 | 5-6 | | | | |

 Table 4: Fastness properties of untreated and treated wool fabrics before and after dyeing

Where: A = alteration, C = staining on cotton, W = staining on wool

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