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Investigation on Durability of Copper Nano Particles on Cotton Fiber

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Abstract

In recent years, metal nano particles such as silver, copper and zinc have developed in textile finishing. Copper nano particles are used in wound dressings and socks to give them antibacterial properties. In the present paper, cotton fabrics were treated with different concentrations of Cu nano particles colloidal solution. For investigation of the durability of nano particles on cotton fabric, laundering test was carried out. Antibacterial activity, wetting time, bending length, crease recovery angle and whiteness were investigated. Cu ions contents on cotton fabric were determined using atomic absorption spectroscopy and the chemical bonding was detected using the FTIR/ATR spectroscopy. The scanning electron microcopy was used for surface morphology studies. The results showed that increase of copper nano particles concentration increased antibacterial activity, and after repeated laundering, some of copper nano particles were removed from the fabric so that bacteria reduction reached to 92 %. Whiteness decreased by Cu nano particles coating. Increase of copper nano particles concentration increased crease recovery angle, bending length, wetting time. Atomic absorption analysis showed the decrease of copper ion content after repeated laundering.

Keywords: *Antibacterial activity, Cotton, Cu ion content, Copper nano particles.*

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Introduction

Carbohydrates in cotton can act as a source of nutrients for microorganisms under certain conditions [1 – 3]. The growth of microorganisms on textiles leads to the generation of unpleasant odor, discoloration, fiber damage and staining, and it can be minimized during their storage and use. The textiles can be treated with antimicrobial finishes to prevent these unpleasant effects [1]. Heavy metals act as antimicrobial agents and kill microbes by binding to intracellular proteins and inactivating them [4 – 6]. Several antibacterial agents of textiles based on metal salts solutions have been developed [7 – 9]. Copper has been used for antimicrobial finishing of textiles [1, 6]. Copper has potential industrial applications, such as gas sensors, catalytic processes, high temperature superconductors, solar cells, conductive films, lubrication and nanofluids [10, 11]. Copper metal inhibits the growth of bacteria, fungi and algae. Copper nanoparticles are used in wound dressings and socks to give them antibacterial properties [10 – 14]. It has been noticed because of its antibacterial properties [10, 15 – 17] and can be used in sterilization of hospitals, microbicidal agents [10, 18 – 23].

In recent years, scientists are interested in nanotechnology researches, because of the change in the substrate properties when their size is reduced to the nanometers range [24, 25]. The effect of nanotechnology in textile finishing has led to innovative finishes [26]. Different nanomaterials like copper, zinc, titanium, magnesium, gold, alginate and silver have developed [27 – 31]. Applications of some metal nanoparticles on textiles were also reported in the literatures [25, 32 – 33]. Chattopadhyay synthesized nano-sized colloidal copper and showed the effect on some properties of cotton fabric such as tensile, bending, crease recovery, dyeing fastness and antimicrobial activity; they found that Cu nanoparticles enhanced the dyeability of cotton with direct dyes. Both the wash and light fastness of direct dyed cotton were upgraded due to Cu nano pre-treatment [25]. Bajpai investigated the antibacterial activity of copper nanoparticles loaded alginate-impregnated cotton fabric [34].

The aim of the present research was to investigate durability of copper nanoparticles on cotton fabric at different concentrations of Cu nano particles. The cotton fabric was treated with different concentration of Cu nano particles. For determination of the durability of Cu nano particles on cotton fabric, laundering test was carried out. Physical properties such as wetting time, bending length, crease recovery angle and whiteness were investigated. The antibacterial properties and Cu ions contents on cotton fabrics were determined using AATCC-100 standard test method and atomic absorption spectroscopy, respectively. The chemical bonding was detected using the FTIR/ATR spectroscopy.

Experimental

Materials

The fabric was a desized and bleached plain weave 100% cotton fabric weighting 143.3 g/m^2 with 85 warps and 65 wefts in inch. The Cu nano colloidal solution (40 – 50 nm) was from Nano Pars Co. in Iran. SDC standard detergent (without optical brightener) was used. The nitric acid was from the Applichem Industries, Germany.

Methods

The plain weave cotton fabric was immersed in Cu colloidal nanoparticles solution at different concentrations of 0.01, 0.03, 0.05, 0.1, 0.2, 0.5, 1 % (owf %) at temperature of 80 °C for 30 minutes, then dried and rinsed. The laundering test was done according to the AATCC standard test method 124 for 5 cycles of washing at temperature of 47 °C for 30 minutes.

The antibacterial test was carried out according to the AATCC standard test method 100. The AATCC 100 test method evaluates the antibacterial activity of antimicrobial finishes on textile materials.Two kinds of bacteria (*Escherichia coli, and staphylococcus aureus*) were used for the test, and the samples were incubated for 24 hours. After 24 hours of bacteria growth, the photos were taken from agar plates, then colonies were counted and bacteria reduction was calculated from the equation:

$$\text{Reduction}(\%) = \frac{\text{C}-\text{A}}{\text{C}} \times 100 \qquad (1)$$

Where C is the counted colonies of cotton fabric and A is the counted colonies of Cu nanoparticles coated cotton fabric.

Wetting time of untreated and treated fabrics was determined according to the AATCC – 39 – 1980 standard test method. A drop of distilled water was poured from the burette on the surface of the fabric. The time for disappearing of spherical shape of water drop was determined. The distance between the tip of burette and the surface was 10 mm. The mean for 10 measurements were reported.

Crease recovery angle of untreated and Cu nanoparticles treated cotton fabrics was determined using the AATCC – 66 1990 standard method. The bending test was carried out according to the ASTM – D1388 standard test method.

The color parameters of treated fabrics were obtained using (X-rite color eye 7000 A) reflectance spectrophotometer. The three coordinates (L*, a*, and b*) of CIELAB color system were obtained and whiteness was calculated (Standard Illuminant D65/10°).

The Cu ion content on cotton fabric was determined by atomic absorption spectroscopy. The certain amount of cotton fabric was placed in furnace (Nabertherm, Germany) at temperature of 600 °C for 1 hour, and then was diluted to a certain volume. The copper ions were determined from the calibration curve of standard solutions and were reported in terms of gram per 100 grams of fabric.

Infrared spectra were collected using a Bruker-Equinox 55 system FTIR ⁄ATR (Fourier transform infrared spectroscopy/ Attenuated Total Reflectance). All data were recorded by means of a ZnSe Internal Reflective Element. Spectra were collected at a resolution of 4 cm^{-1} and 32 scans.

The surface morphology of the untreated and Cu nanoparticles treated cotton fabric were investigated using the scanning electron microscope of KYKY, EM3200 model of China. The samples were coated with gold before taking the micrographs. The magnification of micrographs for nanoparticles was 40000×.

Results and discussion

Antibacterial activity

Chattopadhyay showed that Cu-nano treatment enhanced the resistance of cotton towards microbial attack when measured in terms of loss in breaking load due to soil burial test [25]. Antimicrobial activity of metal nanoparticles can be attributed to the small particle size of the metal ions and their high specific surface area. Their large specific surface area enables a large increase in the concentration of metal cations released from the particle surface, which results in increased biocidal activity. The mechanism of nanoparticles is based on oxidative stress, which causes damage to the lipids, proteins and DNA of the microorganisms [1 – 3, 35].

Figures 1 and 2 demonstrate the bacteria reduction percentage of Cu nanoparticles treated cotton fabrics with two kinds of bacteria (E. coli, S. aureus) after and before laundering. The untreated cotton fabric was used for control fabric and the Cu nanoparticles treated cotton fabrics were compared with it. It can be seen that by increasing copper nanoparticles concentration the bacteria reduction increased. Heavy metals display a certain degree of sterilization. Copper nanoparticles act as an antibacterial agent and are used for killing microbes and bacteria [25, 36]. Therefore increase of copper nanoparticles concentrations leads to higher bacteria reduction, so that it reached to 99 % of bacteria reduction for E. coli and 98 % for S. aureus at 1% (owf) of copper nanoparticles. After repeated laundering, antibacterial activity decreased to 92 % for both of bacteria. This is due to the removing copper nanoparticles by 5 cycles of washing process.

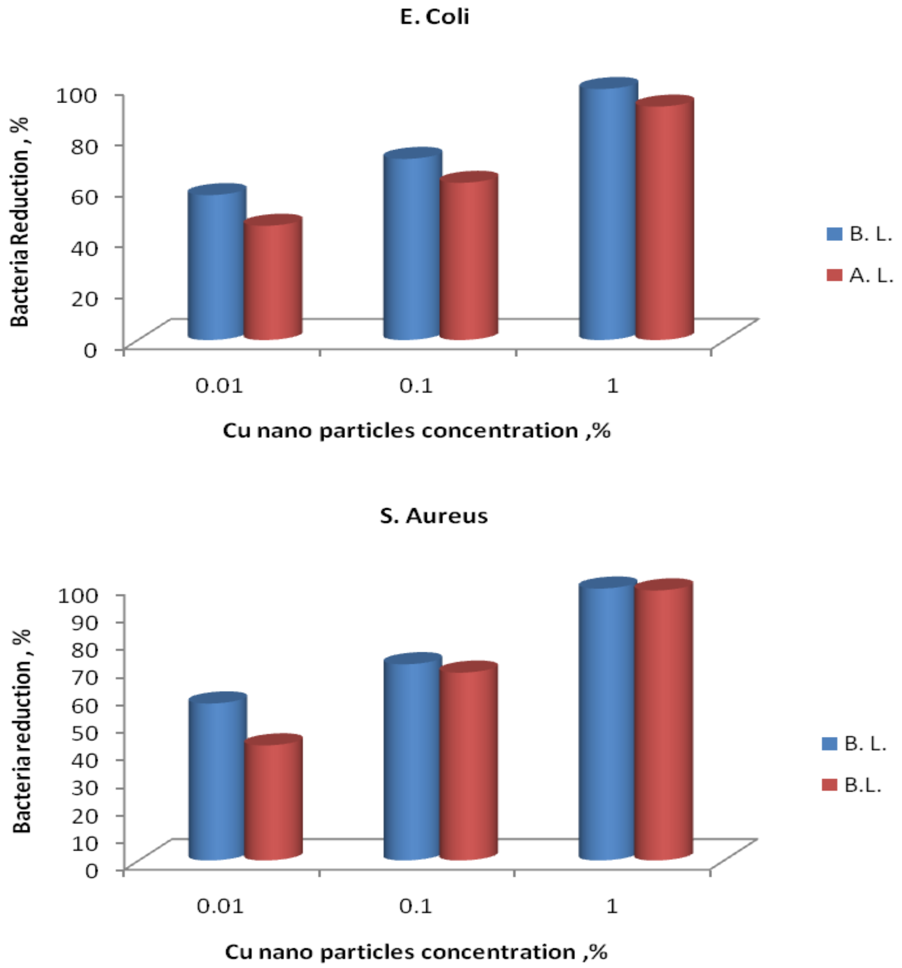


Figure 1. Antibacterial activity of copper nanoparticles coated fabric with two bacteria (E. coli, S. aureus).

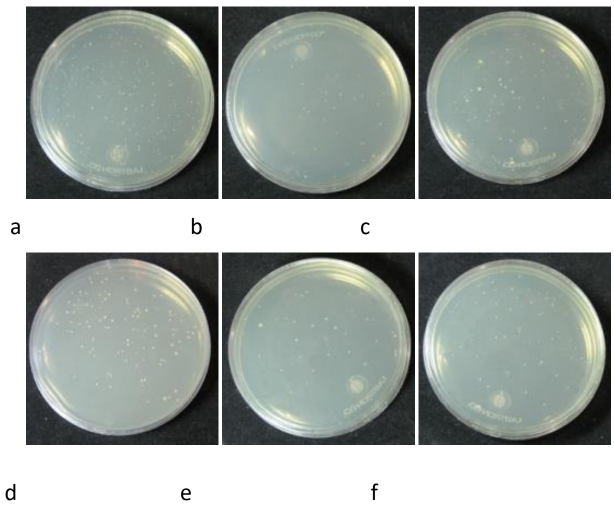


Figure 2. a – E. coli colonies on untreated cotton; b – nano copper treated; c – nano copper treated after laundering; d – S.aureus colonies on untreated cotton; e – nano copper treated; f – nano copper treated after laundering.

Wetting time

Table 1 shows wetting time, bending length and crease recovery angle results of untreated and Cu nanoparticles loaded cotton fabric at different concentrations of copper nanoparticles. The untreated fabric showed the wetting time of 4.39 s. By loading the Cu nanoparticles on cotton fabric the wetting time increased to 4.54 s for the concentration of 0.01 %, and wetting time increased by increase of copper nanoparticles concentration to 6.43 s. This increase was in agreement with the previous works of the researchers. The presence of the particles on the surface of fabric prevented of penetrating the water drop into the fabric. The particles made a rough surface so that blocked the penetration of water drop. After repeated laundering, the wetting time decreased (Table 2) as compared with before laundering, because of the decrease of nanoparticles on the fiber surface. The nanoparticles were removed from the fabric surface by washing process. The removed particles were attributed to the physically absorbed particles which did not have any reaction with fiber. The other reason for increasing water absorption time was, penetrating nanoparticles between the molecules, fibers and yarns structure which prevented of water penetrating by filling the free space between the molecules and fibers [25].

Table 1. Wetting time, bending length and crease recovery angle of untreated and Cu nanoparticles loaded cotton fabric at different concentration, before laundering.

Cu nano particles, %	Wetting time, s	Bending length, cm	Crease recovery angle
–	4.39	18.75	124.25
0.01	4.54	18.96	134.625
0.03	4.66	19.62	136
0.05	4.86	19.75	144.25
0.1	5.35	20.12	145.25
0.2	5.74	20.22	145.75
0.5	6.12	20.50	147.5
1	6.43	20.93	149.25

Table 2. Wetting time, bending length and crease recovery angle of untreated and Cu nanoparticles loaded cotton fabric at different concentration, after laundering.

Cu nano particles, %	Wetting time, s	Bending length, cm	Crease recovery angle
–	3.39	20. 9	124.25
0.01	3.54	21.18	130.25
0.03	3.68	21.43	134.25
0.05	3.72	22	138.75
0.1	3.75	22.43	140.5
0.2	3.84	22.5	143.75
0.5	3.86	22.82	144
1	4.09	23	148

Bending length

The bending strength test of fabric shows the flexibility and stiffness of the fabric. When the bending length increases the fabric becomes stiffer whereas decrease of bending length shows softness of fabric. The bending length for untreated and Cu nanoparticles loaded cotton fabric are shown in Table 1. The bending length increased by increasing the concentration of Cu nanoparticles, so that it reached to 20.93 cm at concentration of 1 % of Cu nanoparticles. The nanoparticles created a rough surface on the fabric surface and the fabric became stiffer, they also penetrated into the fiber structure and reduced the flexibility of the fiber, slightly change happened in bending length of fabric [25]. After repeated laundering the bending length of nanoparticles treated cotton fabrics reached to 23 cm for 1 % of Cu nanoparticles (Table 2). The increase of bending length after repeated laundering was due to the shrink behavior of cotton by washing process which affected on bending length of fabrics, Although we expected the decrease of bending length because of the removing the particles from the fiber. After repeated laundering, the bending length reached from 21.18 cm to 23 cm by increasing Cu nanoparticles concentration.

Crease recovery angle

Table 1 shows that the crease recovery angle (CRA) of untreated cotton fabric was 124.25, and by loading the Cu nanoparticles at concentration of 1 % it reached to 149.25. The increase of Cu nanoparticles concentration slightly increased the crease recovery angles. The nanoparticles penetrated into the fiber and between the cellulose structures. These particles caused the non-flexible and rigid fiber which increased the stiffness of the fiber and fabric [8]. The copper nanoparticles entered between the molecules of polymer and acted as filler or cross-linking agents. Cross linking agents caused improvement in crease recovery and increases rigidity [25], but slight change happened by increasing copper nanoparticles concentration.

Whiteness

The used copper nanoparticles colloidal solution had a yellow brown color which might affect on the color of cotton fabric. Therefore, the whiteness of untreated and copper nanoparticles treated cotton was investigated. Figure 3 shows whiteness of Cu nanoparticles treated cotton fabrics. The whiteness reduced by increasing of Cu nanoparticles concentration, therefore the fabric became more yellow because of the adding Cu nanoparticles solution.

After repeated laundering, whiteness increased and fabrics became whiter. Some of the copper nanoparticles, which were attributed to the physically absorbed particles, were removed from the fiber by repeated washing. The remained particles in fiber might be attributed to the chemically bonding to the fibers, or it might be removed by extra washing. These results were in agreement with the antibacterial results which showed decrease of antibacterial effect of copper nanoparticles treated cotton fabric by repeated laundering.

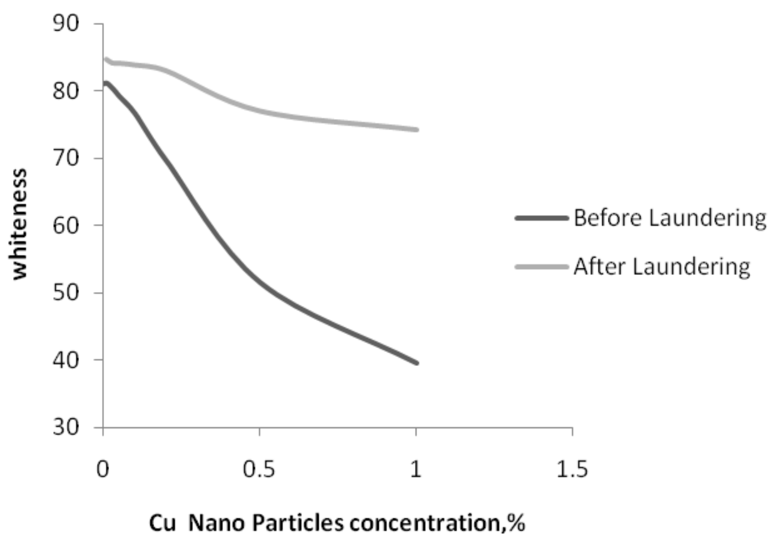


Figure 3. Whiteness of Cu nanoparticles coated fabrics after and before laundering.

Atomic absorption analysis

For determination of copper nanoparticles content on cotton fabric, atomic absorption analysis was used. Figure 4 shows the results of atomic absorption analysis, the Cu concentration per 100 grams of fabric versus Cu concentration on treatment solution. By increasing the Cu nanoparticles in treatment solution, the copper ion content increased in fabric. After repeated laundering the copper nanoparticles concentrations decreased. This was due to the removing the non-absorbed particles during the repeated washing process. The mechanism of Cu nanoparticles attraction was according to physically and chemically absorption of nanoparticles, which physically absorbed particles, was removed from the fiber by repeated washing process. The remained particles in fiber might be attributed to the chemically bonding to the fibers that might be the attraction between hydroxyl groups of cellulose and positive charge of Cu nanoparticles.

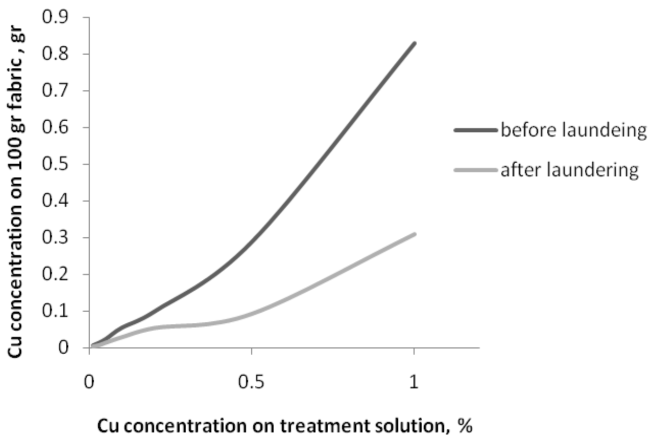


Figure 4. Cu content on 100 grams of fabric before and after repeated laundering.

FTIR/ATR analysis

Figure 5 shows FTIR/ATR spectra of untreated cotton and copper nanoparticles treated cotton fabrics. The spectrum of untreated cotton showed stretching bond at the region of 3500 cm^{-1} was related to hydroxyl groups of cellulose which was disappeared on copper nanoparticles treated cotton fabric, and the stretching bonding of 1720 cm^{-1} increased for the copper nanoparticles treated cotton. The stretching bond at 1720 cm^{-1} was due to the carbonyl groups [37]. These results indicated the attraction of Cu ion to carbonyl groups of cellulose.

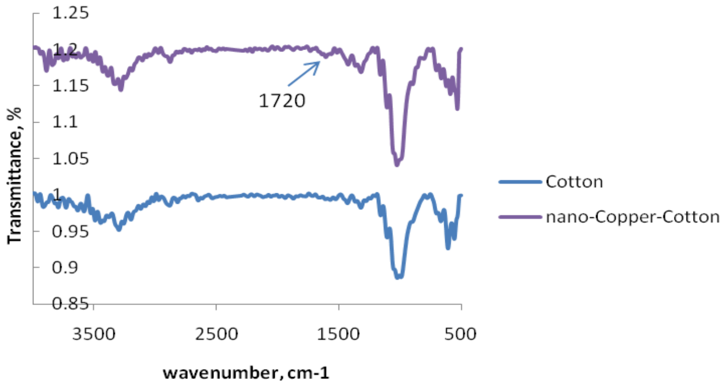
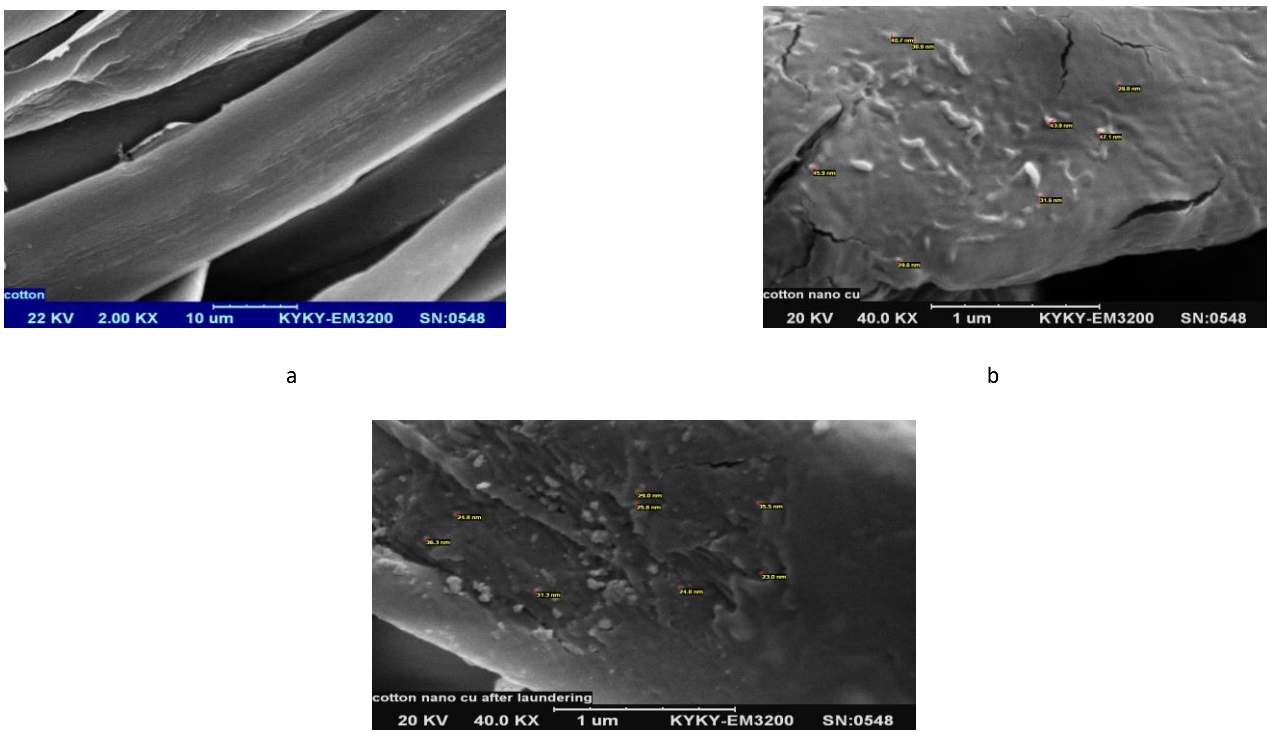


Figure 5. FTIR/ ATR Spectra of cotton and copper nano particles treated cotton fabric.

Scanning electron microscopy

Figure 6 demonstrates the SEM micrographs of copper nanoparticles loaded cotton fabrics before and after laundering. The nanoparticles of copper with the size of less than 50 nm were shown in the micrographs after and before laundering. Some of the copper nanoparticles were shown on the surface of the fiber, and some of them might penetrate into the fiber structure which affected on increase of some physical properties such as bending length, crease recovery angle, wetting time. Since the scanning electron microscopy is not a quantitative test for determination of nanoparticles we cannot judge about the amount of nanoparticles on cotton fabric before and after repeated laundering.



a

b

c

Figure 6. SEM micrographs of: a – un-treated cotton; b – nano Cu treated cotton before laundering; c – after laundering.

Conclusion

Copper nanoparticles act as an antibacterial agent and are used for killing microbes and bacteria. For household usage of copper nanoparticles on textiles, which undergoes washing processes, the durability is important. In this research, the increase of copper nanoparticles concentrations led to higher bacteria reduction. After repeated laundering, antibacterial activity decreased to 92 % for both of bacteria. Atomic absorption analysis also showed the decrease of copper ion content after repeated laundering. This was due to the removing copper nanoparticles by washing process. The removed particles were attributed to the physically absorbed particles which did not have any reaction with fiber.

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