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Green Synthesis Copper Nano Particles for Increasing Antibacterial Properties of Polyester Fabrics.

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ABSTRACT

In this study, a new method was introduced for surface modification of polyester fabric by synthesizing copper nano plates using copper sulfate, glucose and sodium hydroxide. Copper sulfate reacted with sodium hydroxide in the presence of glucose resulted in deposition of copper nano plates on the fabric surface. The main point was simultaneous synthesis of copper nano plates and fabric surface modification in one step and simplicity of the procedure. The treated fabrics could be used in diverse areas such as defense, aerospace, electronics, medical and health industries. Surface characteristics of the fabric samples were investigated through observation of surface morphology by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). Also, chemical structure was identified by FTIR and concentration of nano plates in the solution was determined by UV-Vis absorption. The fabric reflection spectra showed copper nano plates with thickness of 30-40 nm loaded on the polyester fabric. The results of antibacterial tests indicated that the samples treated with nano-copper had an excellent antibacterial activity against both E. coli and S. aureus as reduction of bacteria up to 100% in the modified fabric.

Keywords: *In situ* synthesis, nano plates, polyester fabric, copper, glucose, antibacterial.

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INTRODUCTION

Use of metal nanoparticles is currently highly regarded due to their useful properties. Using nano metals on textile causes development of new properties and characteristics on the fabric that is produced as a result of metal characteristics. In the past two decades, considerable studies have focused on synthesis of metal nanoparticles in order to find potential applications. Decrease in particle size leads to increase in surface to particles' volume rate with high increase in catalyst features of metal nanoparticles. Chemical catalysts can effectively improve performance and structures by multiple productions of particles and strong chemical bonds between the matrix and particles cause some structural strength and increase [1, 2]. Copper and its compounds have been studied for many years, not only for their antibacterial activity, but also for their low toxicity [3-10]. Several methods have been developed for preparing copper nanoparticles, which include photo-catalytic reduction, chemical reduction, photo-chemical or radiation–chemical reduction, metallic wire explosion, sono-chemical, polyols, matrix chemistry, photo-reduction, reverse micelle based methods and even biological synthesized[11]. Among various metal particles, use of copper nanoparticles has been highly considered due to their availability, low cost and optical, electrical, catalytic, mechanical, magnetic and conductive properties[12].

In previous studies of nano-metal materials such as copper have been synthesized by various methods such as prepared in an aqueous solution using sodium dodecyl sulfate as capping agents[13, 14] . A method for synthesizing copper nanoparticles has utilized charge compensatory effect of ionic liquid BF4 in conjunction with ethylene glycol for providing electro-steric stabilization to copper nanoparticles prepared from copper sulphate using hydrazine hydrate as a reducing agent [15] . with an additional coating of a hydrophilic polymer has been carried out using hydrazine hydrate (HH) and sodium formaldehyde sulfoxylate (SFS) in an aqueous medium[16].

Metal nanoparticles such as Ag and Cu are found to have antibacterial activity [17, 18]. Bactericidal effect of metal nanoparticles has been attributed to their small size and high surface to volume ratio, which allow them to closely interact with microbial membranes, which is not merely due to release of metal ions in solutions [18, 19].

Antibacterial properties of metal nanoparticles have found applications in various fields such as medical instruments and devices, water treatment and food processing. Antibacterial effect of copper nanoparticles was reported by Yoon et al. [18, 20]. reported antifungal and bacteriostatic properties of copper nanoparticles[18, 21].

In this study synthesis of nano copper and surface modification of the polyester fabric is carried out in one step. The role of glucose as stabilizer in this method and thus copper sulfate reactions with sodium hydroxide at presence of glucose resulted in creating copper nano plates and their deposition on the fabric surface.

MATERIALS AND METHODS

Instrumentation

Materials

The applied materials were obtained as follows: polyester fabrics with 165 g/m^2 from Hijab Co. (Iran). Copper sulfate ($CuSO_4$*$5H_2O$) and Sodium hydroxide (NaOH) and glucose has been prepared from Merck Co. (Germany) were used.

Machines

Absorption rate of nano copper was studied by a spectrometer called Varian, Cary100 UV-Vis-NIR. Reflection spectra of nano copper on the fabrics were investigated by a Spectrophotometer Color-Eye 7000A (USA) and antibacterial test. Surface morphology of the fabric was observed by scanning electron microscope TESCAN VEGA 5130 mm SEM/EDX (Britain). To determine chemical groups on the fabric, and FT-IR spectrometer (model Bomem-mb100) was (Germany) used. Also, crystal structure of the fabric was

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investigated by an X-Ray diffraction system (model XRD PTS 300) from SEIFERT Co. (Germany). Tensile properties of fabric measured Testometric M500-25CT. (UK)

Methods

The accuracy synthesis of copper nano plates in both. Then, Polyester fabric samples were prepared at 10*10 cm and washed using standard method in a washing bath including a non-ionic detergent 1 g/L and sodium carbonate 1g/L at 60°C for 20 min. The samples were washed and then dried. The main step which included nano copper synthesis bath was performed by impregnation of the sample in the bath containing copper sulfate 0.05%, sodium hydroxide and glucose 0.01% at 100 °C for 120 min. The samples were then taken out and dried at 100°C for 4 min followed by curing at 150°C for 3 min. The finished fabrics were washed and their properties were investigated.

Synthesis of nano copper in solution

The copper nano plates synthesized by bath containing copper sulfate, polyester fabric, sodium hydroxide, glucose as reducing agent. Therefore, in the method, synthesis of copper nano plates and deposition onto the fabric in one-steps. Copper nano plates were formed and physically attached to the polyester fabrics.

The possible mechanism of reaction of copper sulfate with sodium hydroxide and glucose as reducing agent has been shown in Reaction 1, 2 and 3 and. This can be done through the chemical and physical reaction that leads to formation of fabrics.

$$CuSO_4{*}5H_2O + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4 + 5H_2O \quad (1)$$

$$Cu(OH)_2 \xrightarrow{\text{Heating}} CuO + H_2O \quad (2)$$

$$10\ C_6H_{12}O_6 + 120\ CuO \xrightarrow{\text{Heating}} 120\ Cu + 60\ CO_2 + 603\ H_2 \quad (3)$$

Synthesis of nano copper on polyester fabric

In situ synthesis, the conversion Cu^+ to Cu^0 is possibly by reducing agents and substitution of Cu^+ with H^+ can be due to the higher positive chemical potential of Cu^+ (+0.34). Also Copper nano plates were physically linked on the compact structure of the polyester fabric. (Fig.1).[22, 23] by initiation of nano copper synthesis on polyester fabric, they Grown and particle size have been bigger.

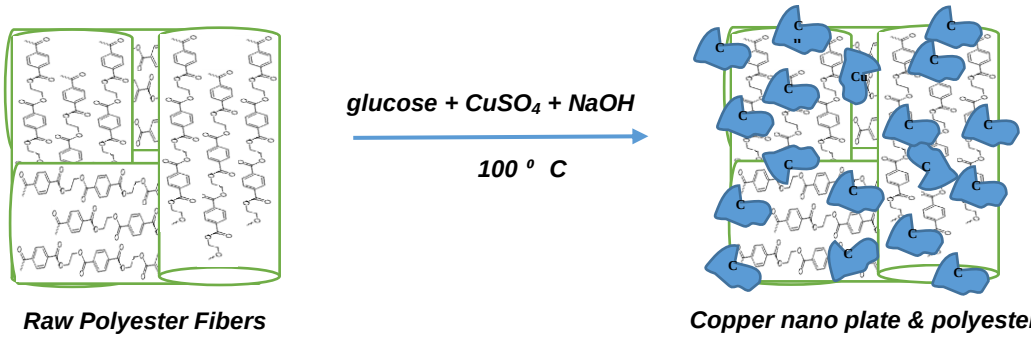

Figure 1: Polyester fabric finished with copper nano plate

Absorption spectrometry

In this experiment, the remaining solution of the treated samples was separated and analyzed using a Cary 100 (Fig.2), which revealed a peak around 600- 650 nm that confirmed synthesis of nano copper [24, 25].

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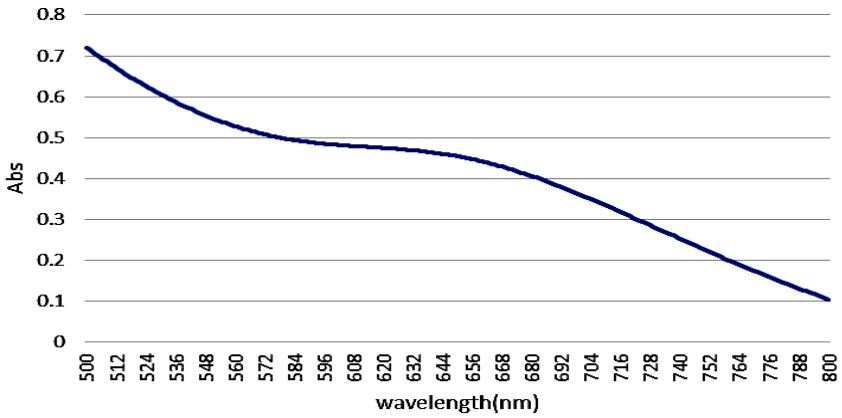

Figure 2: Absorption spectrum of the remaining solution

Reflection spectrometry

The treated polyester fabrics with nano copper and raw samples were analyzed using reflective spectrometer (Fig.3), through which the amount of ΔE was calculated. Also, a significant peak was observed in the range 550-650 nm, which was not present in the raw samples, indicating the presence of copper nano plates on the surface of the fabrics [26].

Also, copper diffusion into the polyester samples and reducing agent caused changes in the color of polyester samples. The changes of color indicated variations ranging from 1.8 to 3.6. Thus, the processing conditions were influenced on the color changes. Mild conditions caused low changes in color and hard conditions produced bigger changes in polyester color. This parameter should be optimized with other parameters such as tensile and others.

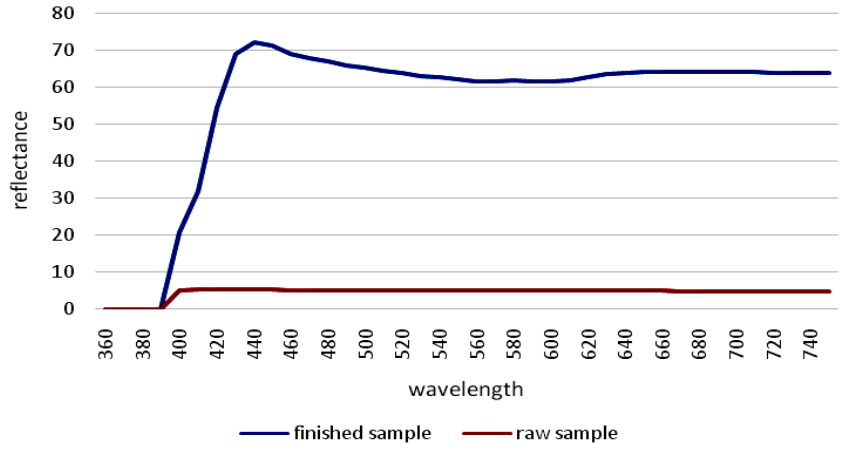

Figure 3: Reflectance spectroscopy of the samples modified and raw

X-ray diffraction (XRD)

XRD is a simple instrument to determine unit cell size and shape for each combination. Diffraction methods are useful for qualitative analysis (phase identification), quantitative analysis (determining lattice parameter and analyzing phase fraction) and diffraction pattern (Fig.4) [24].

The XRD peak positions were consistent with metallic copper. Sharp peaks of the XRD pattern indicated the crystalline nature. The peaks at 43.38°, 50.44° and 74.125° corresponding to the Miller indices (111), (200) and (220), respectively, represented face centered cubic structure of copper. Lattice constant of the unit cell was a=3.615 Å and its volume was 4.7245×10^{-29} m^{-3}[18].

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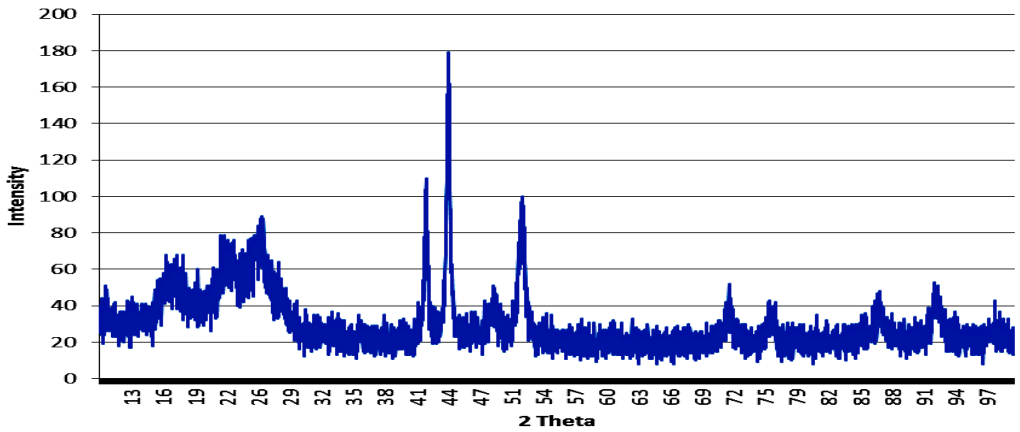

Figure 4: X-ray diffraction of polyester fabrics modified

The synthesized nano plates were found to be phase-pure copper without any impurity phase such as CuO, Cu_2O and $Cu(OH)_2$. In order to do this, the treated sample was placed using Kv/30 mA data of 2 theta from 10 to 100 degrees and amount of 2 theta was found as shown in Table 1[18].

Table 1: 2 theta of synthesized copper nano plates on polyester fabric

2theta	Int	d(A°)
44.36	179	2.0880
51.6	100	2.5118
75.88	34	1.4779

Their crystal structure was analyzed by XRD using Cu-Kα ray (γ=0.154 nm) within the range of 10 to 100 degree angle at 0.02 degrees in each registered step. The particles' average size was estimated by calculating width of the peaks created in the samples by means of sheerer formula:

$$D=0.9\lambda / \beta \cos \theta$$

(Where β= peak's width at half of maximum, λ= length of X-ray radiation, θ= angle between radiations' open ray and radiation, d= particles' size).

In the SEM figure such as sheerer formula observed copper nano-plates on the fiber surface with thickness of 30-80 nm.

FTIR

Infrared spectroscopy is done based on absorption of radiation and evaluation of vibrational mutation of multi atomic molecules and ions. This method is used mainly for detecting organic compounds because spectra of these compounds are usually complex and have a minimum and maximum number of peaks that can be used for the purposes of convention. FTIR in wave number range of 500–4000 cm^{-1} used to prove the effectiveness of the processing conditions on the molecular structure of the treated polyester samples[24].

Fig. 5 shows the chemical groups present in the fabrics before and after modification. The changes observed in the peaks showed alteration in the fabric chemical structure through the synthesis of nano copper. Standard IR Absorption Frequencies in table 2 is shown [27-29] . But, the synthesis of nano copper on polyester caused changes in some peaks. Carbonyl groups peaks of samples were shifted between10 and 20 cm^{-1} and some of ester groups peaks shifted depending on the experiment conditions. The changes can be related to the types of reducing agent and processing conditions. Therefore, the shift in peaks indicated nano copper synthesis changes due to the extension of polyester. (Fig.5-a, 5-b).

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Table 2: IR peaks identified by wave number peak location [27-29].

Peak	Peak location (cm^{-1})
C=O	1730-1750
C-O	1000-1300
CH2 wagging mode of trans conformer of glycol moiety	1340
Trans configuration of ethylene glycol unit	975
Gauche configuration of $–OCH_2CH_2-$ group	896
Benzene ring	795

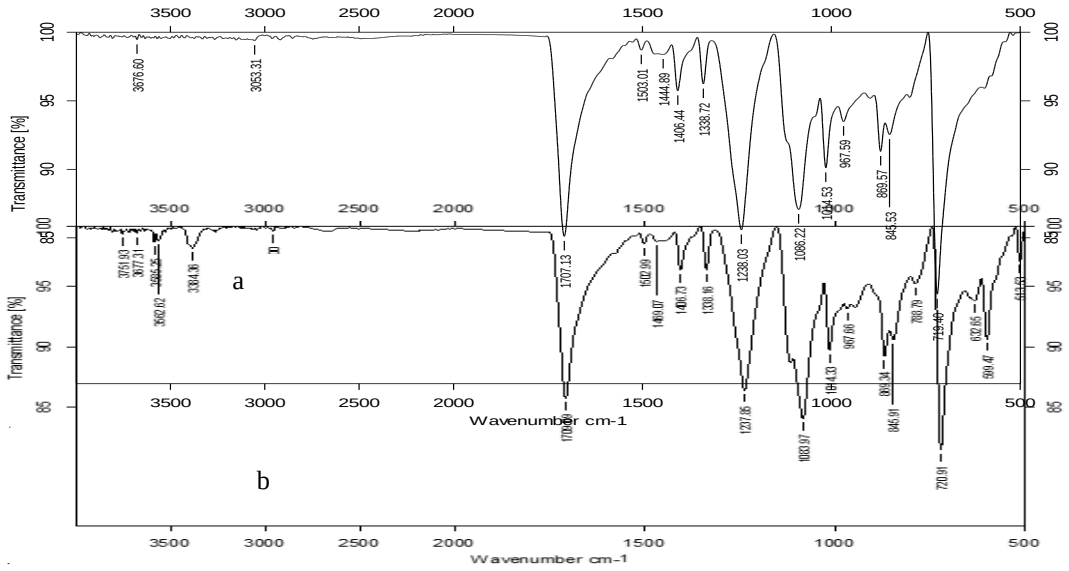
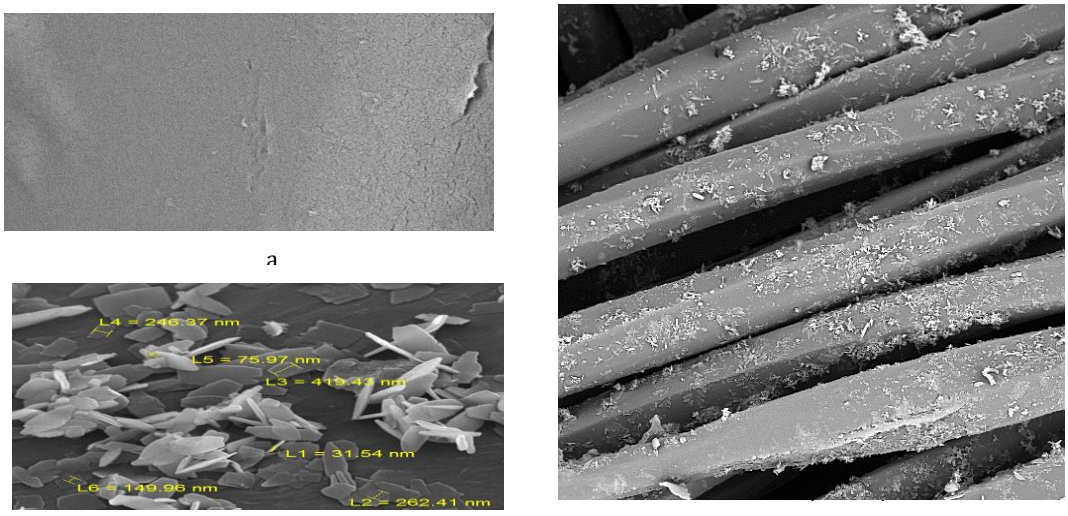


Figure 5: FTIR spectrum of various fabrics: a) raw and b) modified with copper nano-plates

SEM/EDX

Surface morphology could be determined by means of electron microscope and analyzed by means of analyzer. Non-conductive materials are usually covered with a thin layer of carbon or gold for taking pictures. SEM proved synthesis and loading of copper nano plates on the polyester fabrics as indicated in Fig. 6. Nano materials were observed in the shape of nano-plates on the fiber surface with thickness of 30-80 nm.



a

b

c

Figure 6: SEM images of different fabric samples: a) raw with 20000X, b) finished with nano copper 1000X, c) finished with nano copper 20000X,

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The samples were analyzed by EDX to show elemental composition of the samples (Fig.7). EDX results presented in Table 3 that it confirmed the presence of nano copper on the polyester fabrics and also proved the influences of the processing conditions on the copper content on the polyester surface. The copper nano plate on the polyester fabrics surfaces in the range of 1.29% synthesized. The EDX results caused more synthesis of nano copper on polyester fabrics.

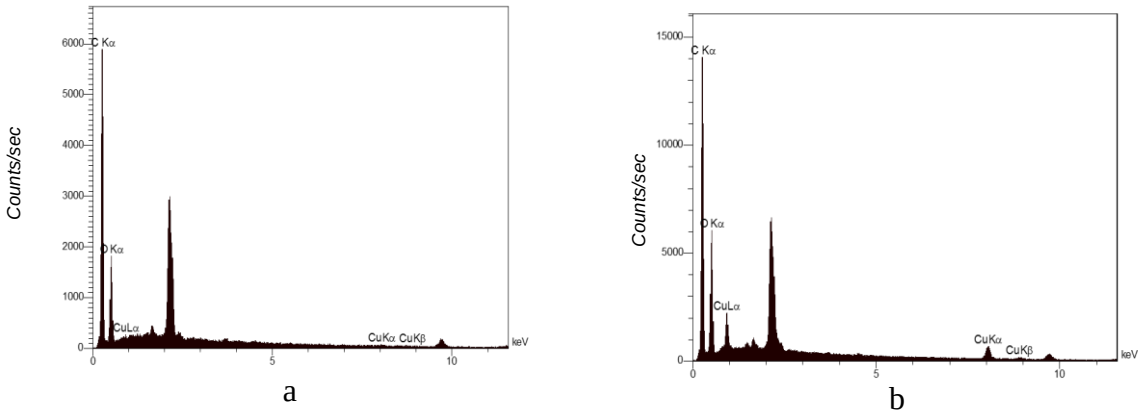

Figure 7: EDX patterns of: a) raw and b) modified polyester with copper nano plates

Table 3 shows atomic and weight percentages of different elements on the fabric sample. Only carbons and oxygen groups were observed on the raw samples which were related to the polyester groups; but, on the finished samples, copper In addition to carbon and hydrogen groups was found.

Table 3: Wt. % and A% elements on the polyester fabric of: a) raw, b) modified with copper nano plates

a. Raw sample			
Elt	Line	W%	A%
C	Ka	65.45	71.62
O	Ka	34.55	28.38
Cu	Ka	0.00	0.00
		100.00	100.00

b. Modified sample			
Elt	Line	W%	A%
C	Ka	58.20	67.97
O	Ka	34.76	30.48
Cu	Ka	7.04	1.55
		100.00	100.00

Antibacterial

The large particles could be easily removed from the fiber surface while small particles could penetrate into the fabric matrix and adhere stronger on the fabric surface[30]. This issue could perfectly confirm higher antibacterial properties, residual Copper, UV blocking and washing durability in alkali modified fabrics [31] . The number of bacteria colonies on the agar plate before and after the nano treatment was counted and the results reported as percentages of bacteria reduction according to AATCC 100-2004
Test method and

a $$R(\%) = \frac{A - B}{A} \times 100$$ b

where (A) and (B) are the numbers of bacteria colonies recovered from the untreated and the treated samples respectively after incubation and (R) is the reduction percentage of bacteria colonies[32] .

Table 4: Antibacterial activity

No	Name of the organism	Sample Nano copper treat	(R %)
1	*Staphylococcus aureus*	++	98.6
2	Escherichia coli	++	99.7

Tensile strength and weight properties

Sodium hydroxide is quite shallow activity on polyester fabrics and shortens the polymer chains, a Thinning and create voids on the surface of the fiber[33, 34]. Weight loss polyester fabric with alkaline hydrolysis as a good way to improve the appearance and aesthetic properties of these fabrics, which reduce weight by 10% to 30% polyester is very desirable and Help to in situ synthesis of nano copper is the polyester fabric[34].

The use of sodium hydroxide increased the strength of the samples is in the bath copper nanoparticles. Increase the Tensile Strength of samples treated in the presence of copper nanoparticles by linking with functional groups on the surface of polyester and also desire to Aggregation Nanoparticles within the cavity created by the alkaline hydrolysis is due to the surface of polyester[34].

This test has been shown to increase the tensile strength of 6.48% and also the weight loss was observed around 2.35%.

CONCLUSIONS

This study showed successful treatment of polyester fabric with copper salt to synthesis copper nano plates on the fabric surface to increase their applications. Also, this paper explored a new method of in situ synthesis of nano copper within polyester fabrics. Availability and simplicity of the procedure were unique characteristics in this study. The synthesis of nano copper confirmed by SEM, EDX and XRD patterns on polyester fabrics. Also the synthesis of nano copper in the solution confirmed with UV visible absorption spectra. Further, the reasonable antibacterial properties indicated on the fine polyester fabrics on both S. aurous and E. coli. And the nano copper finishing agents could really kill the bacteria not just inhibit their growth. Overall, 6.48% enhance in tensile strength, 3.2 color change and 2.35% weight loss with good antibacterial properties. This study of glucose was used as a stabilizer agent. Thus copper sulfate reactions with sodium hydroxide in the presence of glucose at 100 ^{o}C for 120 min resulted in creating copper nano plates and their deposition on the fabric surface. The results indicated formation of copper nano plates with thicknesses of 30 to 80 nm that mostly were physically link on the compact structure of the polyester fabric.

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