Effect of Nanosized Colloidal Copper on Cotton Fabric

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ABSTRACT

This research deals with the synthesis of nanosized copper as colloidal solution and its application to cotton fabric. Copper nano colloids were prepared by chemical reduction of copper salt using sodium borohydride as reducing agent in presence of tri-sodium citrate. The size and size distribution of the particles were examined by particle size analyzer and the morphology of the synthesized particles was examined by SEM and AFM techniques. X-ray fluorescence spectroscopy detected the presence of copper in the treated fabric. The results of particle size analysis showed that the average particle size varied from 60 nm to 100 nm. The nano copper treated cotton was subjected to soil burial test for the assessment of its resistance towards microbial attack. SEM images of treated fabric indicate copper nano particles are well dispersed on the surface of the specimens. The treatments of nano copper colloidal solution on cotton not only improve its antimicrobial efficiency but also influenced the tensile strength of the fabric sample positively. The treatment was found to enhance the color depth and fastness properties of direct dyed cotton fabric samples.

Keywords: Absorption spectrum, Bacterial resistance, Copper, Cotton, Dyeing, Nanoparticles

INTRODUCTION

The fundamentals of nanotechnology lie in the fact that properties of substrates dramatically change when their size is reduced to the nanometer range. Moreover, a small amount of nanosize species can interfere with matrix polymer that is usually in similar size range, bringing up the performance of resultant system to an unprecedented level.

The textile industry, among other leading industries, is also an area in which nanotechnology is being implemented with full enthusiasm [1]. Nanotech-textiles are on the way of becoming the most popular textiles with their protective, functional and electronic features. One of the most important advantageous features of nanotech-textiles is their protective properties.

The unique properties of metal nano particles are well known. Nano metals like Au, Ag, Pd, Pt, Zn etc were synthesised by many workers [2-3]. Applications of some of these particles on textiles were also reported in the literature [4-6]. Beside well known antimicrobial property of Ag nano particle, Chattopadhyay and Patel showed that silver nano particle treatment could improve the tensile strength and color depth on cotton, wool and silk fabric [7]. Information on synthesis cum application of Cu nano particles on textile material is hardly found in the literature. The present study was, therefore, aimed at synthesizing nano copper particles by a suitable method and investigating its effect on the properties of cotton fabric.

EXPERIMENTAL

Fabric

Mill scoured and bleached 100 % cotton fabric with following specifications was used in this study; Plain weave with a weight of 238g/m² and a density of 44 threads/cm in the warp and 28 threads/cm in weft directions.

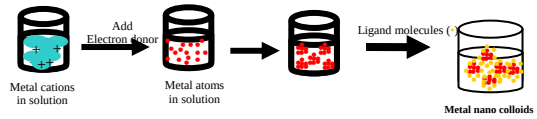
Dyes and Chemicals

Three commercial direct dyes namely, C.I. Direct red 9 (X), C.I. Direct blue 67 (Y) and C.I. Direct Green 6 (Z) were selected for this study without any purification. Silver sulphate Copper sulphate ($CuSO_4.5H_2O$, M.W.249.68), sodium borohydride ($NaBH_4$, M.W.37.83) and tri-sodium citrate ($C_6H_5Na_3O_7.2H_2O$, M.W.294.10) of analytical grade purity were procured from Sd Fine Chemicals, (India).

Equipment

Copper nano were synthesized in specially designed reaction chamber with N_2 gas supply. The particle size and size distribution was analyzed on particle size analyzer (Malvern instrument, MAL501131, DTS version 5.03, U.K.) Atomic Force Microscope (easy Scan 2 Nanosurf AG, Switzerland.) operating in a contact mode (cantilever force constant 3 N/m) was employed for visual observation of the particles. The particles were also imaged through Scanning Electron Microscope (SEM), (model JSM5610LV, version 1.0. Jeol, Japan). The amount of copper as element in the polymer structure was detected and measured using an X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The operating X-ray source voltage and current were 35 kV and 26 mA respectively. Registration time was 30 s and the investigated area was 78.5 mm^2.

Application of synthesized nano on cotton and dyeing of nano treated fabric was carried on a constant temperature shaking water bath (Alliance enterprise, India). After dyeing the color strength in terms of *K/S* values were recorded on Spectra scan 5100 (RT) spectrophotometer, (Premium Colorscan Instruments, India). The washing fastness of the fabric was performed on launder-ometer (Digi.wash, Paramount Scientific Instruments., India). Light fastness was carried out on Xenon arc Fad-ometer, (FDA-R, Atlas, U.S.A.).



Scheme 1

SCHEME 1 Schematic process diagram of copper nano colloid synthesis

The 100 ml solution of copper sulphate ($CuSO_4.5H_2O$, 0.3 gm, 4.17 mmol in 100ml water) kept in the specially designed reaction chamber, was slowly reduced by drop wise addition of very dilute chilled solution of sodium borohydride ($NaBH_4$,, 0.1gm, 3.83 mmol in 50ml water) in a nitrogen atmosphere. During the process of reaction the solution mixture was stirred vigorously. As the color of the solution turned to light yellow 5 ml of trisodium citrate ($C_6H_5Na_3O_7.2H_2O$, 0.1gm, 29.41mmol in 100ml water), were added drop by drop with vigorous stirring. Distilled water was used for preparing the solutions of all the chemicals. *Scheme 1* gives schematic picture of Cu nano particle formation and their stabilization by citrate anions.

Nano Cu Treatment on the Cotton Fabric

The synthesized nano cu dispersion was applied to cotton fabric using exhaust method at 40°C and liquor to material ratio of 50:1. After 1 h, the temperature was increased to 80°C over 30 min. the treated fabric samples were thoroughly washed, neutralized and dried in air.

Determination of Tensile Properties

Cotton fabrics were tested for the change in their tensile properties before and after nano treatment. The breaking load of the samples was determined on tensile tester instrument (LRY model, Lloyd, U K)

Determination of Crease Recovery Angle

The crease recovery angle of the samples was determined as per AATCC Test Method 66-2003 using Sasmira crease recovery tester (India).

Determination of Bending Length

The stiffness in terms of bending length of nano treated and untreated samples were measured as per AATCC Test Method 115-2005 using Prolific stiffness tester (India) for the measurement of bending length.

Dyeing of Untreated and Treated Cotton

All dyeing were carried out in a laboratory dyeing machine at liquor to material ratio of 20: 1, in the presence of 10–50 g/l of sodium chloride and 20 g/l of sodium bicarbonate using 2.0% dye on the weight of the sample. The sample was treated at 50°C for 10 min. The temperature was slowly raised to boil over 30 min and the dyeing was continued at boil for further 45 min. After samples were wash in cold running water for 30 minutes.

Evaluation of Dyed Samples

The effect of nano Cu treatment on the dyeability of cotton in terms of *K/S* was measured on computer color matching system Spectra Scan 5100 (RT) spectrophotometer interphased with computer color matching system.

Fastness Testing

The dyed sample was tested according to ISO standard methods. The specific tests used were: ISO 105-CO6 (C2S) for color fastness to washing; ISO 105-BO2 (1990) for color fastness to light.

Evaluation of Antimicrobial Activity

The untreated and treated samples were subjected to soil burial test as per AATCC Test Method 30-2004 [8]. After the stipulated period the samples were removed from soil, washed thoroughly with water and dried in air. The samples were then tested for breaking load on tensile tester.

RESULTS AND DISCUSSIONS

Copper nano particles were prepared by reduction of copper salt and stabilized with citrate anions. The nano cu particles in the solution were analyzed by particle size analyzer. The particles were also observed using SEM and AFM instruments .The presence of Cu was detected and measured by X-ray fluorescence spectrometer.

The formation of synthesized nano Cu was noticed by the change in the optical properties of the reaction solution. The optical properties of metal nanoparticles depend strongly upon the particle size and shape [9]. The blues-green color of $CuSO_4$ solution gradually changes to intense yellow when the particle size of copper reduced to nano level [10]. These effects are the result of the changes in the so-called surface plasmon resonance [11], the frequency at which conduction electrons oscillate in response to the alternating electric field of incident electromagnetic radiation. However, only metals with free electrons (essentially Au, Ag, Cu, and the alkali metals) possess plasmon resonances in the visible spectrum, which give rise to such intense colors. The aggregation of the particles was controlled with the help of citrate anions. The copper nano colloidal particles formed a negative surface charge due to the adsorbed citrate ions. Each sphere of Cu nano particles surrounded by citrate ions therefore repelled each other and prevented further aggregation.

The particle size and size distribution of the prepared and stabilized Cu colloid were analyzed on Malvern instrument. *Figure 1* shows the intensity size distribution of Cu nano particles dispersed in water.

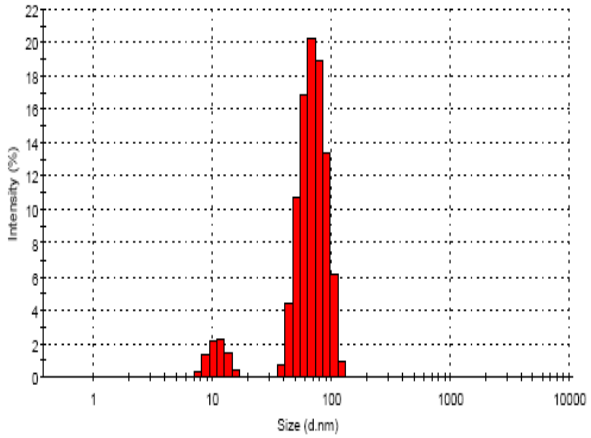


FIGURE 1. Particles Size and their distribution for synthesized Cu nano colloids

Figure 2 shows the scanning electron micrographs of stabilized Cu nano particles deposited on carbon coated aluminum sheet.

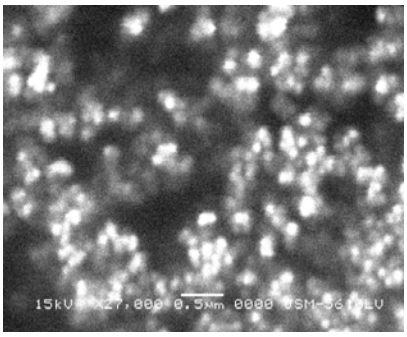


FIGURE 2. Scanning Electron Microscope (SEM) images of synthesised copper nano particles

The average size as seen from the scale of the photograph is about 60-100 nm which is also in agreement with the size distribution found using particle size analyzer. It can also be seen from the picture that the shape of synthesized particles is spherical.

The copper nano particles were deposited on glass plate for observation under atomic force microscopy (AFM). The size of nano Cu particles as seen from the scale on the AFM image (*Figure 3*) and topography lies below 100 nm, which also supports the results, obtained using particle size analyzer.

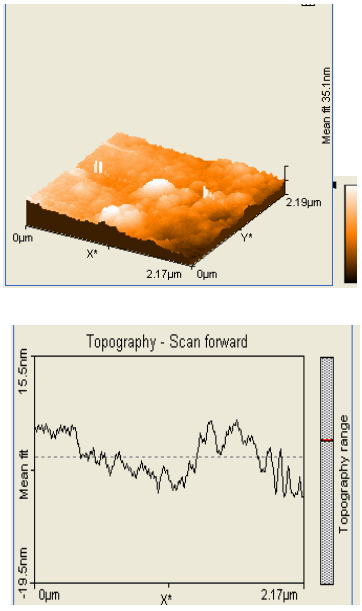


FIGURE 3. Atomic Force Microscopic image and topography of synthesized Cu nano colloids

Both the treated and untreated cotton were elementally analyzed using X- ray fluorescence spectroscopy for the detection and measurement of elemental copper.

TABLE I. Amount of copper detected with XRF

Structure	Amount of copper, µg
Cotton	Nil
Cu/Cotton fabric	0.19

The results given in *Table I* show that the amount of copper found on treated cotton was about 0.19 µg against nil for untreated one.

The effects of nano Cu treatment on the physical properties of cotton were examined and presented in *Table II*. It is seen from the results that introduction of nano copper particles into the structure of the fiber caused an improvement in the load bearing capacity of the fiber. The treatment could raise the breaking load of cotton by about 71%.

The nano copper particles because of their small size can enter in between the polymer molecules and perhaps act as fillers or cross linking agents which also contribute to the load sharing phenomenon during load application to the material. Unlike chemical cross linking which causes an improvement

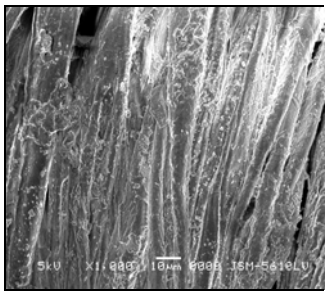
TABLE II. Effect of cupper nano treatment on physical properties of cotton sample.

Sr. No.	Sample	Breaking load (kg)	Crease recovery angle °(deg)	Bending length (cm)
1.	Untreated cotton sample	8.02	90	1.05
2.	Cotton pre-treated with cu nano particles	13.75 (+71.44)	99 (+10.00)	1.50 (+42.86)

Note: Values in the parenthesis indicate percentage change in physical properties.

in crease recovery angle at the cost of imparting some rigidity in the material to an extent depending on the extent of cross linking, the incorporation of nano copper particles remained quite gentle in this regard. There was little improvement in crease recovery angle of the fiber with a little increase in bending length. Therefore though the particles entered in between the polymer chain molecules did not interfere much to the polymer flexibility of the system, the treatment was thus devoid of harshness to the material.

a) Untreated cotton fabric



b) Copper nano treated cotton fabric

FIGURE 4 Scanning Electron Microscope (SEM) images of (a) Untreated and (b) Treated cotton fabric.

From the SEM microphotograph of nano Cu treated cotton sample (*Figure 4b*), it can be clearly seen that the Cu nanoparticles are distributed on the surface of the treated cotton sample.

The Cu nanoparticle treated cotton fabric sample was dyed with three direct dyes and compared with the untreated samples. The *K/S* values of the nano copper pre-treated samples were found to be higher (*Table III*) than the corresponding untreated samples of cotton. The maximum improvement in color strength was observed with direct green 6 dye.

TABLE III. Effect of Cu nanoparticles on dyeing of cotton fabric with direct dyes

Sample	**Dye**	***K/S***
Untreated cotton sample	X	5.32
	Y	8.22
	Z	8.06
Cotton pre-treated with cu nano particles	X	7.36 (+38.34)
	Y	11.35 (+38.08)
	Z	13.17 (+63.39)

Note – Values in the parenthesis indicate percentage change in *K/S*, X – C.I. Direct Red 9, Y – C.I. Direct Blue 67 and Z –C.I. Direct Green 6

TABLE IV. Effect of Cu nanoparticles on the fastness properties of cotton fabric dyed with direct dyes.

Sample	**Fastness rating**								
	Light			**Washing**					
	X	**Y**	**Z**	**X**		**Y**		**Z**	
				A	**S**	**A**	**S**	**A**	**S**
Untreated cotton	3	3	3	2-3	2	2-3	2-3	2-3	2
Cu-nano treated cotton	4	4	4-5	4	4	4	4	4-5	4-5

Note X; Direct Fast Pink BD, Y; Direct Blue B, and Z; Direct Green 6, A; Change in depth, S: stain on cotton

The higher *K/S* values of nano treated samples indicate that the presence of nano metal particles increased the dye affinity towards the material. The copper nanoparticles in the fabric thus acted as mordant. The negatively charged dye anions got attracted towards the fiber probably due to the polarity developed in the metal particles by induction which resulted in better bonding between the dye and the fiber. The better coupling of the dye and fiber is also reflected in the improvement of the color fastness properties (*Table IV*). Where the Cu-nano treated / untreated and dyed fabrics after washing off using 2 g/l non-ionic detergent, the Cu-nano treated and dyed sample was almost remaining unaffected by the wash-off procedure. Thus copper nano pre-treatment not only improved the color strength but also improved the color fastness which is a major drawback of most direct dyes.

TABLE V. Effect of Cu nanoparticles on resistance of cotton bacterial attack

Sample	Breaking load		
	Before soil burial	After soil burial	% Change
Untreated cotton sample	8.02	6.50	-18.93
Cotton pre-treated with Cu nano particles	13.75	11.71	-14.80

Note – Values in the parenthesis indicate percentage change in *breaking load.*

Antimicrobial activity was measured by soil burial test and the results are shown in *Table V*. It is clear that the Cu-nano treatment was found to enhance the resistance of cotton towards microbial attack when measured in terms of loss in breaking load due to soil burial test. The breaking load of untreated control samples were reduced due to bacterial damage during soil burial test whereas copper nanoparticle treated sample could not only protect the sample against bacterial attack but also improved its strength. Metallic ions and metallic compounds display a certain degree of sterilizing effect. It is considered that part of the oxygen in the air or water is turned into active oxygen by means of catalysis with the metallic ion, thereby dissolving the organic substance to create a sterilizing effect [12]. With the use of nano-sized particles, the number of particles per unit area is increased, and thus antibacterial effects can be maximized.

CONCLUSIONS

The nanosized copper colloidal solution were prepared successfully and applied to cotton fabric; The average particle size was found to be about 60 nm. Cu nano treatment on cotton has been shown to improve the tensile strength of cotton fiber with little improvement in crease recovery angle and bending length. The Cu nano treatment was also found to enhance 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. Cu-nano treatment also increased the resistance to microbial attack. Copper nano treatment thus increased the effective life span of the treated fabric.

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