PREPARATION AND DEPOSITION OF COPPER NANOPARTICLES ON CELLULOSE AND THEIR ANTIBACTERIAL PROPRIETY

A. GUESMI[a,b], K. TAHA[b], A. HOUAS[b], N. B. HAMADI[b,c,*]
[a]*Textile Engineering Laboratory , Higher Institute of Technological Studies of Ksar Hellal, UM (University of Monastir), Tunisia*
[b]*Chemistry Department, College of Sciences, IMSIU (Al Imam Mohammad Ibn Saud Islamic University), Riyadh 11623, Kingdom of Saudi Arabia*
[c]*Laboratory of Synthesis Heterocyclic and Natural Substances, Department of Chemistry, Faculty of Sciences of Monastir, Boulevard of Environment, 5000 Monastir, UM (University of Monastir), Tunisia*

Synthesized copper nanoparticles were deposed on cotton by using Arabic gum. Several analysis methods were used to detect the presence and to characterize the produced nanoparticles. Analyses results shown that the Cu_2O nanoparticles were distributed above the entire surface of the textile fiber. The discharge of nanoparticles in the washing bath was characterized by atomic absorption, and results confirmed the equitable durability of the treated cellulose. A study on mechanical properties of the cotton@nanoCu_2O composite was developed and revealed that treated cotton preserves interesting physical properties. The antibacterial effects of cotton@nanoCu_2O composite have been tested, and was in overall excellent.

(Received November 25, 2018; Accepted January 10, 2019)

Keywords: Copper, Gum Arabic, Nanoparticles, Cotton fiber, Antibacterial

1. Introduction

Nowadays, the commercial market for antibacterial textile materials has grown rapidly due to the increased awareness and need of consumers. As known, polymeric materials, such as cotton and wool, affords an exceptional substrate for bacterial growth under the appropriate environmental conditions [1-3]. Microbial multiplying eventually causes damage to the polymeric material and also induces human infections [4,5]. A number of antibacterial agents are used to improve the resilience against microorganism [6]. The copper nanoparticles have been extensively applied to fiber materials due to their strong antibacterial and inhibitory properties. Those interesting properties results from the large contact areas with microorganisms [7,8]. The antibacterial properties of copper nanoparticles are especially dependent on their shapes and sizes. Consequently, advanced technologies have been used to assure a uniform size distribution of nanoparticles. Current studies have shown that the smallest particles sizes confer better antibacterial properties than the larger particles [9]. Several materials have been associated to copper nanoparticles in order to increase the antibacterial activity of fibers [10]. For example, silver nanoparticles produced by fungi on cotton fibers revealed that they exhibit a strong antibacterial activity against Staphylococcus aureus [11]. In this developed study, we report a new in situ preparation method of synthesis of CuO nanoparticles on the surface of a natural fiber, by exhausting gum Arabic. Antibacterial properties of CuO nanoparticles fixed on textile fibers have been studied.

* Corresponding author: ahlemguesmi@ymail.com

2. Materials and methods

2.1. Materials and chemicals

Materials

Textile materials

Scoured and bleached cotton fabric, of 150 g/m^2, was treated with a solution containing 1 g/L of a non-ionic detergent (Hostapal CV, Clariant). Treatment was carried out at 95 °C for 30 minutes. Finally, the fabric was washed with water and air dried at room temperature.

Gum Arabic

Two natural mature gums (GA1 and GA2) and commercial gum GA3, collected successively from acacia and apricot trees, and grown in Tunisia were kept for further usage.

Chemicals

All reagents in this research were purchased from MERCK, Germany, and Across Organic, New Jersey, USA, and were used as received.

Chemicals were $CuSO_4 \cdot 5H_2O$ (99%), NaOH (99%) and hydrazine hydrate (35% hydrazine).

Methods

Characterization of gum Arabic

The molecular parameters of gum Arabic was measured using gel permeation chromatography online coupled with multiangle laser light scattering system (GPC-MALLS, Wyatt Technology Corp., USA), results are summarized in Table 1.

Preparation of coated cotton fibers with CuNPs.

Synthesis of CuNPs

CuNPs were prepared according to previously published processes with slight modifications (). 3 mL of a prepared solution of $CuSO_4 \cdot 5H_2O$ in ethylene glycol (0.01 M) was mixed with 3 mL of a solution containing 1 mL of 0.005 M NaOH and 2 mL of 0.015 M $N_2H_4 \cdot H_2O$.

The whole was treated under magnetic stirring. After 5 minutes, the resulted mixture was sonicated at 50 W for ten minutes. After treatment, the color of the whole mixture was varied from blue to brick red. The mixture was then cooled to room temperature, and distilled water was added. At the end, the solution was filtered to obtain the product. The obtained solid was excessively washed with distilled water, ethanol and acetone and was then placed in a vacuum oven and dried at 60 $^{\circ}$C for 2 hours [12]. The product was directly used.

Preparation of treated cotton fibers

Gum solutions were prepared by dispersing different weights of powdered gum (0.25, 0.5, 0.75 and 1 g) in 100 mL of distilled water. Cotton fibers (5 cm × 5 cm, 1 g) were added to the gum solutions. The resulting mixture was kept in an Ahiba machine and treated at 80 °C for 40 min. The treated samples were finally dried at ambient temperature.

Coating of Cu_2O nanoparticles into cotton fibers

A mass of 0.1 g of nano-copper particles was added to 50 mL of distilled water. The pretreated cotton fiber (5 cm × 5 cm, 1 g) was then added to the resulting solution. The overall was stirred at a temperature of 40 °C for 30 min. Cotton fabric was finally removed and rinsed thoroughly in tap water and then dried at ambient air.

Tensile strength and elongation at break (%)

The tensile strength and the elongation at break, for the untreated and the treated fibres, were determined according to the ASTM D5035 strip test.

Atomic absorption spectrophotometry

The quantification of the adsorbed Cu on cotton fabric was conferred by measuring the concentration of the residual Cu in the solution obtained after the dissolution of cotton fibers.

The dissolution of cotton was achieved by immersing about 10 to 20 mg from the coated cotton sample into 1 mL of concentrated H_2SO_4 for 15 minutes at room temperature, followed by an aqueous dilution of the resulting mixture, to reduce the concentration of the acid to 1 M. The overall was then heated at 100 °C for 1 h and finally filtrated through a micro filter.

The amount of Cu was measured in the derived aqueous solution, using a Perkin–Elmer 560 atomic absorption spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT).

Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TECNAI G^2 20 S-TWIN) was used to determine the morphology and dimensions of the Cu_2O nanoparticles. A drop of a diluted aqueous suspension (0.1 wt%) was deposited on the surface of a copper grid coated with a thin carbon film. The sample was dried before TEM analysis, which was carried out with an accelerating voltage of 100-120 kV.

Scanning electron microscope (SEM)

Scanning electron microscope images were obtained with a ZEISS SUPRA40. The electron source, a hot cathode producing electrons by Schottky effect, is a tungsten filament coated with a ZrO layer. A cotton@nanoCu_2O composite was attached on a carbon adhesive and coated with a thin layer of Pt with thickness about 1 nm by sputtering under inert gas.

Antibacterial test

The cotton fibers were tested with two pathogenic bacteria, *Escherichia coli O157:H7* (ATCC 43895), and Staphylococcus aureus MRSA (ATCC BAA-1707). The two strains were initially streaked from a −80 °C glycerol stock on Luria-Bertani (LB) agar (BD biosciences, NJ, USA) plates, and a fresh single colony was then inoculated in LB (25 mL) in 250 mL flasks and cultured at 37 °C with 250-rpm agitation. Overnight cultures were diluted at 1:500 in phosphate buffered saline (PBS). Each cotton fiber disk (0.5 cm diameter) was soaked in 0.3 mL of a diluted bacterial cell solution in a tube and incubated at 37°C for 24 h. For better soaking of the cotton fibers, 0.02% (v/v) polyethylene glycol sorbitan monostearate (non ionic detergent) was added to the mixture of bacteria and cotton disks. After incubation, the surviving cells were calculated as the numbers of colony-forming units (CFUs). All experiments were performed using at least two independent cultures. A disk diffusion assay was completed to test the antibacterial strength visually. Briefly, the overnight cultures of four pathogenic bacteria were diluted to 1:1000 in PBS buffer and 0.1 Ml of each diluted solution was spread on a LB agar plate. Cotton disks were placed on plates and incubated at 37 °C for 24 h. The experiments were performed using at least two independent cultures [13].

2. Results and discussion

Copper nanoparticles were prepared by reducing copper sulfate pentahydrate with hydrazine hydrate in ethylene glycol. A combined system of ultrasound (50 W) and microwave irradiation (100 W) at a temperature of 125°C for 5 minutes was used to prepare those nanoparticles. This method confers stable CuNPs with a narrow particle size distribution that can be saved for several months in air. The prepared copper nanoparticles were characterized using X-ray diffraction and transmission electron microscopy [14]. As seen in (Fig. 1A), the powder X-ray diffraction studies of the precipitates indicated the presence of diffraction peaks located at 2θ values of 43.6, 50.4 and 73.8, which suggested the formation of pure copper. Therefore, XRD studies confirm the formation of CuNPs. Also, the TEM image of CuNPs indicated the presence of nanospheres, and the obtained particle size was varied from 18 to 23 nm (Fig. 1B).

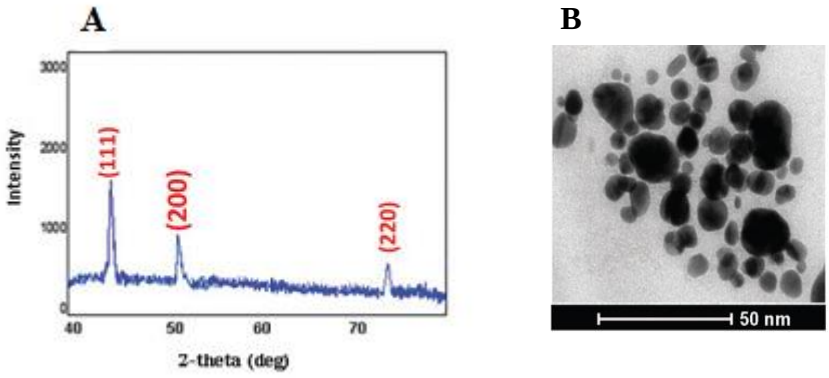


Fig. 1. XRD pattern (A) and TEM images (B) of CuNPs.

Physicochemical properties of gums

Gum Arabic is essentially composed of three components: arabinogalactan protein (AGP), arabinogalactan (AG), and glycoprotein (GP). Three GA were used in this study. The molecular parameters of those three types of gum Arabic are summarized in Table 1 [15].

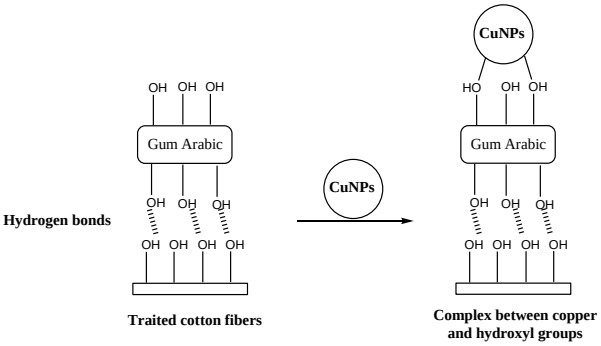
Table 1. Molecular Parameters of GA Measured by GPC-MALLS[a].

	Total fraction	Peak 1, AGP		Peak 2, AG + GP	
Gums	Mw (g/mol)	Fraction (wt %)	Mw (g/mol)	Fraction (wt %)	Mw (g/mol)
GA1	8.35×10^5	12.1	3.19×10^6	87.7	3.65×10^5
GA2	2.89×10^6	17.7	8.79×10^6	80.3	4.45×10^5
GA3	3.90×10^6	29.7	9.77×10^6	70.9	5.35×10^5

[a] GPC-MALLS measurements were carried out at 25 °C using a Superose 6 10/300 GL separation column (GE Healthcare Co., USA) with 0.2 mol/L NaCl as eluent. Peaks 1 and 2 were defined as reported previously.

Characterization of treated cotton fibers

A series of characterization test, on treated cotton fibers, have been suggested in order to prove the effectiveness of the proposed treatment. A suggested scheme for copper nanoparticles attachment with gum Arabic on cotton fibers is shown in Scheme 1.



Scheme 1. Coated of Cu_2O nanoparticles into cotton fibers by complex formation with hydroxyl groups of gum Arabic.

In order to study the effect of the gum Arabic type and concentration on the amount of CuNPs fixed into the treated cotton; a series of test have been developed. Results are summarized in Table 2. As shown, for the three types of gum, a maximum of adsorption of CuNPs into cotton

has been registered in case of cotton pretreated with 0.75 g of gum. It was also observed that the highest CuNPs uptake was registered in case of cotton pretreated with Gum 1; which was previously explained by its glycoprotein content (see Table 1).

Table 2. Amount of fixed CuNPs into cotton.

	Amount of Gums (g)	0	0.25	0.5	0.75	1
Amount of fixed CuNPs (mg)	**GA1**	30	40	70	90	90
	GA2	30	35	50	70	70
	GA3	30	35	40	50	50

UV-Visible Spectroscopy Analysis

UV visible analysis has been used to detect the color modification of treated and untreated cotton fibers, accompanying the treatment process. As seen in Fig. 2, the uv-visible spectra of the cotton@CuNPs present a characteristic absorption peaks around 599–590 nm. The absorption peaks could be attributed to the surface plasmon resonance band of the CuNPs [16].

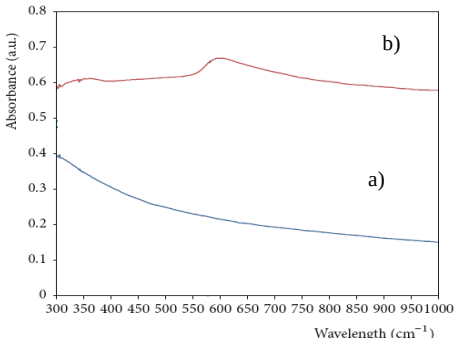


Fig. 2. UV-visible absorption spectra of cotton (a) and cotton@CuNPs (b).

X-Ray Diffraction analysis

The X-ray diffraction analysis was used to investigate the crystallographic behavior of the cotton@CuNPs. As shown if Fig. 3, the two peaks situated at 2θ values of 22.85° and 34.37° for cotton corresponding to the (200) and (004) diffraction planes of cellulose I, still present after the treatment of cellulose. This statement suggests that the fixation of CuNPs on cotton fibers did not change the basic structure of the treated cotton. For the cotton@CuNPs, new peaks situated at 43.38°, 50.52°, and 74.25° are observed. Those peaks are assigned to the diffraction of the (111), (200), and (220) lattice planes of the Cu.

The average particles size of copper nanoparticles can be calculated using Debye-Scherrer equation: where k is the Scherrer constant with the value from 0.9 to 1 (shape factor), λ is the X-ray wavelength (1.5418 Å), $\beta_{1/2}$ is the Width of the XRD peak at half-height, and θ is the Bragg angle. The average particles size of the optimum concentration is found to be less than 20 nm.

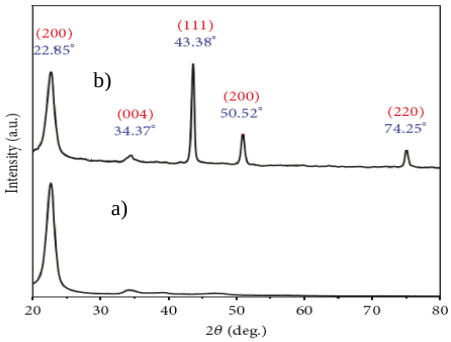
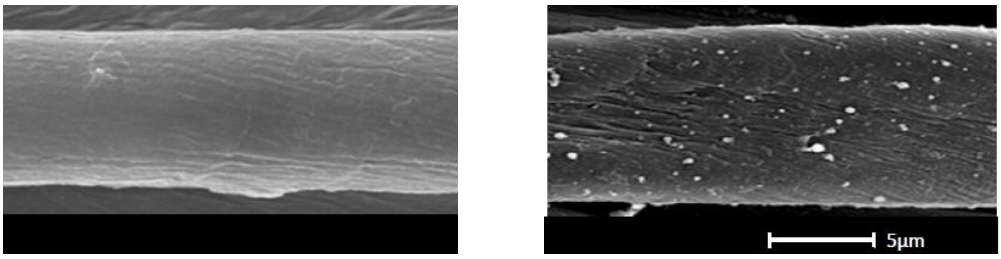


Fig. 3. XRD diffractogram of cotton fibers (a) and cotton@CuNPs fibers (b).

Scanning electron microscope images

SEM analysis has been used to detect the surface modification of cotton later to the treatment. The micrographs of cotton before and after modification are grouped in Fig. 4. As shown, compared to the untreated cotton fibers, the treated cotton present a granular surface appearance, which might be due to the layers of copper nanoparticles coated with gum Arabic on the cotton fibers.



(a) *(b)*

Fig. 4. SEM micrograph of (a) cotton fibers and (b) treated cotton with copper nanoparticles.

Mechanical properties of cotton fabric containing copper nanoparticles

In order to compare the mechanical properties of untreated and treated cotton fabric, the tensile strength and the elongation at break were measured. Results are given in Table 3. As shown, treated cotton preserves interesting physical properties when compared to untreated one.

Table 3. Tensile strength and elongation at break of untreated and treated cotton fabrics.

Fabric	Tensile strength (N)	Elongation at break (%)
Untreated	804.6	21.5
Treated	778.3	18.6

Atomic absorption spectrophotometry

This section has been developed to measure, by atomic absorption spectroscopy, the retention rate of copper on textile fabric treated separately with different Arabic gums. As shown in Table 4, the amount of copper retained on textile fibers depend to their glycoprotein content adsorbed by the pretreated cotton fabric. It is also to note that no copper was leached out during rinsing. This was confirmed by the absence of detectable Cu (by atomic absorption) in the solution after acidic treatment.

Table 4. Correlation between the type of gum Arabic and Cu amount determined by atomic absorption.

Sample	Cu content [a] (µmol/g)	Cu content [b] (µmol/g)
Cotton-GA1- CuNPs	566	0
Cotton-GA2- CuNPs	440	70
Cotton-GA3- CuNPs	314	110

Cu content [a] : Cu content before acidic treatement
Cu content [b] : Cu content after acidic treatement

Antibacterial properties

The antimicrobial properties of cotton@CuNPs was studied by measuring the inhibition zones formed on an agar medium and a direct plating method after the incubation of *E. coli* O 157:H7 and *S. aureus*, along with the textiles at incubation times as presented in Fig. 4. It was shown that the cotton@CuNPs placed on the agar medium killed the bacteria around the fabric. The average diameters of the inhibition zone of *E.coli* O157:H7 and *S.aureus* were 18.4 mm and 18.7 mm, respectively [3].

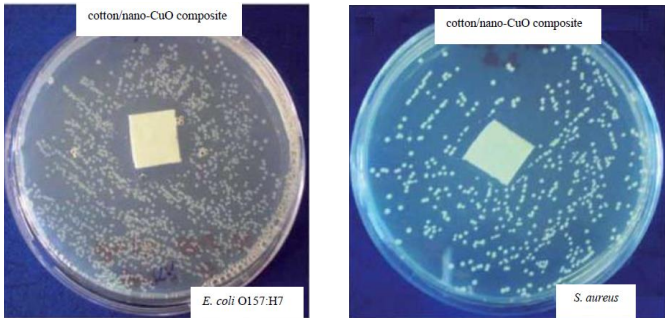


Fig. 4. Antimicrobial activity of cotton@CuNPs.

Through the first 20 min of incubation after bacterial inoculation, the bacterial growth was slightly reduced in presence of cotton@CuNPs. However, after 20 min of incubation, when compared to the growth of the bacteria incubated with normal cotton, the growth of the bacteria incubated with cotton@CuNPs was significantly reduced in an incubation-time dependent manner.

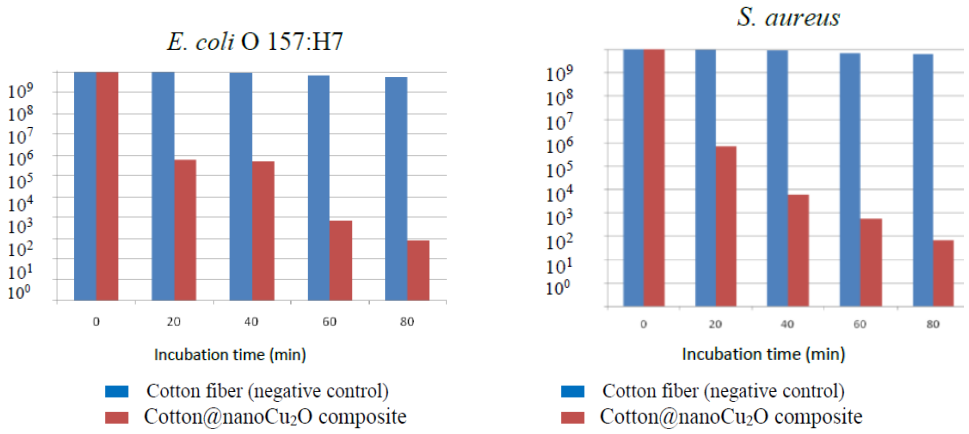


Fig. 5. Growth rate of E. coli O 157:H7 and S. aureus incubated with untreated cotton and with cotton@CuNPs.

3. Conclusions

In this study, we propose the fabrication of an antibacterial cotton fabric through a green and safe procedure developed at room temperature. XRD and SEM analysis of the treated fabric confirmed the nanoparticles distribution on the surface of the fibers. This method proposing the multifunctionalizing of conventional fabrics by using one material is suitable in the industrial scale fabrication.

Therefore, this strategy is estimated to become a powerful platform for the preparation of antibacterial materials. The antibacterial effectiveness of cotton@CuNPs composite is proved notable against both Gram-negative and Gram-positive bacteria through disc diffusion test and quantitative method.

Acknowledgments

The authors extend their appreciation to the Deanship of Academic Research at Al Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh, Kingdom of Saudi Arabia, for funding the work through research project Number 361220, 1436 H.

References

[1] G. Borkow, J. Gabbay, Medical Hypotheses **70**, 990 (2008).
[2] Y. Gao, R. Cranston, Textile Research Journal **78**, 68 (2008).
[3] A. Guesmi, Polymers for Advanced Technologies **27**, 1517 (2016).
[4] A. Deshmukh, S. Deshmukh, V. Zade, V. Thakare, International Journal of Theoretical and Applied Sciences **37**, 781 (2013).
[5] B. Gutarowska, W. Machnowski, L. Kowzowicz, Fibers and Polymers **13**, 415 (2013).
[6] L. Windler, M. Height, B. Nowack, Environment International **53**, 62 (2013).
[7] J. Chen, Y. Luo, Y. Liang, J. Jiang, G. Shen, R. Yu, Analytical Sciences **25**, 347 (2009).
[8] S. T. Dubas, V. Pimpan, Talanta **76**, 29 (2008).
[9] I. Perelshtein, Y. Ruderman, N. Perkas, K. Traeger, T. Tzanov, J. Beddow, Journal of Materials Chemistry **22**, 10736 (2012).
[10] L. Budama, B. A. Cakir, O. Topeal, N. Hoda, Chemical Engineering Journal **228**, 489 (2013).
[11] N. Durán, P. D. Marcato, G. I. H, De Souza, O. L. Alives, E. Esposito, Journal of Biomedical Nanotechnology **3**, 203 (2007).
[12] A. Guesmi, N. Ben Hamadi, Macedonian Journal of Chemistry and Chemical Engineering **35**, 39 (2016).
[13] J. H. Ryu, L. R. Beuchat, Appl. Environ. Microbiol. **71**, 247 (2005).
[14] K. Hajlaoui, N. Ben Hamadi, M. Msaddek, Catal. Lett. **145**, 1246 (2015).
[15] Y. Xiaolin, X. Qiong, T. Dazhi, W. Nana, F. Yapeng, D. Zhongyang, O. P. Glyn, L. Jiang, J. Agric. Food Chem. **61**, 4639 (2013).
[16] K. M. Rajesh, B. Ajitha, K. R. Y. Ashok, Y. Suneetha, R. P. Sreedhara, Materials Today: Proceedings **3**, 1985 (2016).