



Synthesis and Characterization of Freeze Dryer Chitosan Nanoparticles as Multifunctional Eco-Friendly Finish for Fabricating Easy Care and Antibacterial Cotton Textiles



Mahmoud Morsy^{1*}, Khaled Mohamed Mostafa¹, Heba Abdel-Mageid Aryn¹, Amal Abdel-hameed El-Ebissy¹, Ali Mohamed Salah² and Mohamed Adel Youssef²

¹Textile Metrology Laboratory, Chemistry Department, Chemical Metrology Division, National Institute for Standards (NIS), El-Haram, 136, Giza, 12211, Egypt

²Chemistry Department, Faculty of Science, Hellwan University, Cairo, Egypt

ANTIBACTERIAL and easy care characteristics were imparted to cotton fabrics using multifinishing formulation comprising citric acid (CA) and chitosan nanoparticles (CNPs) as an eco-friendly finish. The latter of size around 60-100 nm were prepared through polymerization of meth acrylic acid (MAA) with chitosan using potassium permanganate as initiator and characterized using scanning electron microscope, transmittance electron microscope, Fourier transformer infrared spectroscopy, particle size analyzer, X-ray diffraction and thermo gravimetric analysis. Different factors affecting the degree of multifinishing treatment and their onset on fabric performance and antimicrobial activity were studied and optimized according to pad dry cure method. This was done to see the impact of chitosan nanoparticles to accomplish multifunction characteristics on cotton fabrics like reasonable strength loss, comparable wrinkle recovery angles, elongation at break, higher fabric stiffness and suitable durability in addition to antibacterial activity. It was seen from the attained results that; FTIR spectra and SEM micrograph showed the change in chemical structure and surface morphology of cotton fabric before and after finishing in absence and presence of chitosan nanoparticles. These fabrics parade antimicrobial activity against gram-positive and gram-negative bacteria tested even after 10 washing cycles. Mechanism of finishing of cotton fabric using citric acid and CNPs is identified.

Keywords: Chitosan nanoparticles, Esterification, Tensile strength, Stiffness, Antibacterial effect.

Introduction

Currently nanotechnology inhabits a situation in various fields of anxiety, then it permits manipulating a material at the nanoscale size and modifying final product characteristics [1, 2]. Chitosan is one of the most attractive highly reactive biopolymers mainly due to the presence of amino and hydroxyl functional groups on its backbone structure, such groups embrace also chemical linking of chitosan to organic and inorganic reinforcing network in hybrid preparation. Chitosan is a natural

biopolymer and possess distinctive properties such as biodegradability, non-toxicity, natural abundance, cationic nature, and antimicrobial activity that allow it to be an evocative material for textile industry persistent eco-friendly processes [3, 4]. To obtain more benefits of chitosan, new studies have been focused on nanosized chitosan particles. In textile industry, nanochitosan usage is somewhat new subject and possesses distinctive properties, such as large ratio of surface to volume, surface-active multicenter, high

*Corresponding Author: sayed2008usa@gmail.com

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surface reactivity, excellent physicochemical properties and bioactivity [5-10].

So, several efforts to produce chitosan nanoparticles with different particles size ranged from 175 to 600 nm were studied [11-13]. Meth acrylic acid polymerization is one of the novel likely approaches for fabricating chitosan nanoparticles [1]. Recently chitosan nanoparticles were explored for antimicrobial textile applications as chitosan in the nano form is highly active because of the very high surface area to volume ratio and expected to have desirable bioactivity even at very low concentrations [14, 15, 6]. Besides, chitosan having different molecular sizes were used as a green finish for producing antimicrobial and easy care characteristics to cotton fabrics [16, 17]. Preparation and application of novel chitosan nanoparticles on bioactive polyester fabric to impart enhanced antimicrobial activity at a very low concentration were reported [14]. Also reports [6] studied the effects of chitosan type and nanochitosan concentrations on the anti-bacterial and shrink proofing properties of the wool fabric; the nanochitosan-treated wool fabric possesses better anti-bacterial and shrink-proofing properties. Chitosan nanoparticle dispersion solution as a novel multifunctional agent was also established to modify *Antheraea pernyi* silk [15]. The results revealed that the surface of the chitosan nanoparticle- treated *A. pernyi* silk fiber was rougher than that of bulk chitosan-treated and untreated ones, and a higher specific surface could be achieved. In addition, enhancement in antibacterial activity, breaking strength, and wrinkle-resistance properties of the chitosan-nanoparticle-treated *A. pernyi* silk fabric were also recorded. Nowadays special emphasis on "green chemistry" by researchers is strongly created as a result of increasing awareness about the environment. Utilization of nontoxic chemicals, environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in an ecofriendly synthesis strategy [18-19].

With the above in mind, the present work is undertaken with a view to develop a green synthesis of multi-functional finished cotton fabric. The green synthesis is based on the use of our newly prepared freeze dryer CNPs along with nontoxic citric acid CA to perform dual functions i.e. as crosslinking agent and as anchor

molecules for chitosan fixation on the cotton fabric. Ease of care characteristics likes crease recovery angles and tensile strength as well as comfort likes stiffness in addition to antibacterial activity of the treated fabrics are considered together with other properties affecting the fabric performance.

Experimental

Materials

Mile scoured and bleached plane weave 100% cotton fabric (70 pick X 70 ends/inch, 123g/m²) was kindly supplied by El-Nasr Company for Spinning, Weaving and Dyeing, El-Mahalla Elkoubra, Egypt. Chitosan® (CS) 100 (chipro GmbH, Germany), degree of deacetylation 89.2%, Molecular weight 2.4×10^4 Da was used as a starting substrate to prepare chitosan nanoparticles. Citric acid, sodium hypophosphite potassium permanganate, Meth acrylic acid, and nonionic wetting agent were of technical grade chemicals used throughout the experiments without further purification.

Preparation of freeze drying chitosan nanoparticles (CNPs) via polymerization technique

Polymerization procedure embraces the successive addition of native chitosan to a dilute solution of meth acrylic acid which leads to the polymer suspended on nanoscale via polymerizing MAA in chitosan solution. Unless otherwise indicated, a known weight of chitosan (0.8 g) was dissolved in an aqueous Meth acrylic acid solution (0.5%, wt/v) for 24 h under magnetic stirrer for homogenization. Then, 0.02 mol/l of potassium permanganate as initiator was added to the above solution under continuous stirring at 60°C for 2 h, leading to the formation of CNPs, which were then cooled in an ice bath. The suspension was centrifuged at 6000 rpm for 45 minutes and the supernatant was removed and the settled CNPs obtained from the centrifugation process were further subjected to freeze-drying process.

Freeze-drying of chitosan nanoparticles

Throughout this step, the resulting solution of CNPs was cooled at -60°C for 6 h and ice crystals of pure water were formed. The primary drying stage includes sublimation of ice from the frozen product at 0.07 mbar pressures at -60°C for 8 hours and the secondary drying stage involved the removal of absorbed water from the product at 25°C for 2 h. The obtained

freeze dried CNPs were used for testing and analysis.

Characterization of CNPs via instrumental analysis

Fourier Transform Infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy was carried out using a Nicolet 380 spectrophotometer (Thermo Scientific) and the IR spectra were scanned 32 times over the wave number range of 4,000 – 400 cm^{-1} . The sample (0.002 g) was mixed with KBr to reach (0.2g) to form a round disk suitable for measurements.

Scanning Electron Microscopy (SEM)

SEM images for surface morphology of the samples were taken using (SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification 14x up to 1000000 and resolution for Gun.1n). The surfaces of all the samples were coated with a gold thin layer under vacuum before SEM studies.

Transmission Electron Microscopy (TEM)

TEM images of the samples were obtained using a JEOL (JEM-1400 TEM, Japan), with an accelerating voltage of 100 kV. The CNPs suspension sample was ultrasonically dispersed in deionized water. Then a small droplet of the diluted CNPs suspension was deposited on a 300 mesh copper grid coated with holey carbon film.

Particle size analysis

The average size and size distribution of the CNPs were estimated by dynamic light scattering (DLS) using a Malvern Zetasizer Nano-ZS (Malvern Instruments Ltd., UK) equipped with a He-Ne laser (0.4 m W; 633 nm) and a temperature-controlled cell holder. The mean intensity-weighted diameter was recorded as the average of three measurements in addition to their standard deviations \pm .

X-ray diffraction (XRD)

The X-ray diffraction (XRD) measurements were performed on a PAN analytical Empyrean diffractometer with Cu radiation ($k\alpha_1 = 1.54060 \text{ \AA}$) operated at a voltage of 45 kV and a current intensity of 40 mA. The pattern were recorded by a PIXcel3D solid state detector in the angular range of 5-80° (2 θ) with steps of 0.01° and scan speed of 0.1S0-1.

Thermo gravimetric analysis (TGA)

The TGA analysis was conducted using the

TGA 50 (TA Shimudzu, Inc.). A portion of a whole pellet was cut which served as a single sample. The weight of the sample used was generally in the range of 10 mg. The sample was placed in the equipment and it was heated in nitrogen atmosphere from 20°C to 800°C at a heating rate of 10°C Data showed three distinct weight losses.

Application of chitosan nanoparticles onto cotton fabrics via cross-linking treatment

To optimize the cross-linking treatment conditions, cotton fabrics were padded through two dips and two nips in a solution containing different concentrations of citric acid, chitosan nanoparticles, sodium hypophosphite (50 % based on weight of citric acid), and 2 g/l nonionic wetting agent, in 100 ml double distilled water to a wet pickup of ca. 85%. The fabric samples were dried for 3 min at 85°C and cured at specified temperatures for a specified time intervals in thermo fixing oven (Rapid, H-TS-3). The fabrics were then water rinse and dried at ambient condition before use and were conditioned overnight before characterization.

Characterization of cotton fabric finished in presence and absence of CNPs

Textile testing

Tensile strength and elongation at break

There were measured by strip method in the warp direction using 5 KN universal calibrated testing machine (Tinlus Olsen, model H5KT) according to En ISO 13934-1:1999.

Dry wrinkle recovery angles

It was determined according to ASTM method D-1296-98 using iron recovery apparatus type FF-07 (Metrimplex).

Fabric stiffness

Fabric stiffness in terms of bending length was measured using standard test method ASTM D (1388-966), via measuring bending length (cm) which reflects the stiffness of a fabric when bent in one plane under the gravitational force.

Antibacterial properties

Qualitative method

The assessment of bacteriostatic activity against Gram-positive, *Staphylococcus aureus* (*S. aureus*) and Gram-negative, *Escherichia coli*, (*E-coli*) bacteria was assessed using agar diffusion test according to AATCC test method 147-2004 and expressed as zone inhibition (mm). Fresh inoculants for antibacterial assessment were prepared on nutrient at 37°C for 24 hr. Any

prominent zone of inhibition around the samples was recorded as an inhibitory effect against the abovementioned bacterial species.

Quantitative method

The antimicrobial activity assessment against Gram-positive, *Staphylococcus aureus* (*S. aureus*) and Gram-negative, *Escherichia coli*, (*E-Coli*) bacteria was determined quantitatively according to AATCC 100 test method. The reduction of colonies was calculated using the following equation:

$$R = 100 (B - A) / B$$

Where

R = % reduction

A = the number of bacterial colonies survived after contacting with treated sample and

B = the number of colonies present in untreated control sample (blank).

Durability

The samples were then washed at 40°C in a small washing machine using a solution containing 2 g/l nonionic wetting agent and 1% sodium carbonate. Then, 2, 5 and 10 washing cycles (home domestic laundering washing), 3 min each, were given followed by a water rinse in the same washing machine in accordance with EN ISO 69330 (2005) to test laundering durability. Finally, the fabrics were dried, conditioned, and examined for different properties like tensile strength and dry wrinkle recovery angle after each wash.

Instrumental analysis

Cotton fabrics finished in presence and absence of chitosan nanoparticles were examined by SEM (for fabric surface morphology change), FTIR spectra (for fabric chemical structure confirmation) and Keijeldhal apparatus (for nitrogen content). Nitrogen content of fixed chitosan nanoparticles onto finished fabric was estimated as per a standard Keijeldhal method (Vogel, 1975) using our calibrated instrument model DNP-3000 (Raypa-SPAIN) using standard reference materials.

Statistical analysis

All of the experiments were conducted in triplicate expect that for tensile strength and elongation at break were conducted five times. The data were analyzed and expressed as mean values \pm standard deviations. This was done to insure about the high precision of metrological measurements all over the work when using our

calibrated instruments in our institute either by primary standard apparatus or certified reference materials used especially for this purpose.

Results and Discussion

For simplicity, the results obtained are deliberated under the following headings; (a) preparation of CNPs from native chitosan by polymerization technique encompasses the sequential polymerization of a dilute solution of meth acrylic acid onto chitosan; (b) using CNPs and its booming effect in Nano size scale as multifunctional ecofriendly finish and its impact on fabric performance like tensile strength, elongation at break, dry wrinkle recovery angles, fabric stiffness and durability as well as antibacterial properties; (c) studying the different factors affecting finishing of cotton fabric like citric acid, and CNPs concentrations as well as curing time and temperatures; (d) characterization of finished cotton fabric in presence and absence of CNPs during durable press finishing using the above world class facilities; and (e) antibacterial activity (Qualitative and quantitative) of cotton fabrics finished in presence of different concentrations of CNPs as well as their durability to successive washing.

Fabrication of chitosan nanoparticles via polymerization method

Chitosan molecules together with the polymerization of Meth acrylic acid lead to the formation of cationic polyelectrolyte solution, *i.e.* chitosan–PMAA nanoparticles, *i.e.* (CNPs) via electrostatic interactions as shown in Fig. 1.

Characterization of chitosan nanoparticle (CNPs) Morphology and particle size analysis of (CNPs)

Figure 2 designates the surface morphology and particle size analysis of CNPs prepared from native chitosan using Polymerization Technique via SEM, TEM and particle size analyzer. First, chitosan are generally spherical or oval in shape with relatively smooth surface with a particle size about (3.9 μm) in size when SEM has been used for morphological surface assessment [Figure 2(a)]. The polymerization technique used for the preparation of chitosan nanoparticles through the sequential addition of chitosan to a dilute solution of MAA; leads to the polymer suspended on nanoscale to form the spherical or oval CNPs as shown in SEM image (Fig. 2 b). Furthermore, (Fig. 2c) elucidates also the particle size analysis of CNPs using TEM, while Fig. 2 (d) and (e) showed the particle size analysis obtained from DLS using

a Malvern Zetasizer and the histogram of the size and size distribution obtained from TEM Picture respectively. As is evident from (Fig. 2 (c to e)); using the experimental conditions designated in section 2.2 that leads to the formation of CNPs with smaller particle size ranging from 10 to 190 nm, but with the capacity that the majority of nanoparticles reach an average size between 60-100 nm, which may be really essential for several applications.

FTIR study of chitosan and chitosan nanoparticles

Figure 3 represents the FTIR studies of chitosan and chitosan nanoparticles that implemented to investigate their chemical structure. The native chitosan FTIR spectrum (Fig. 3 a) presents the following characteristics peaks;

- at 3437.33 cm^{-1} assigned to stretching vibration of NH_2 and OH groups,
- at 1648.59 cm^{-1} associated with C=O of amide and,
- at 1082.4 cm^{-1} related to the C–O stretching vibration,

While, for chitosan nanoparticles, the FTIR

spectrum (Fig. 3 b), denotes the absence of the C=O amide band at 1648.59 cm^{-1} , and presence of two new bands at 1633.09 and 1531.69 cm^{-1} assigned to COO^- and NH_3^+ groups, respectively. This is due to the ionic interaction between the carboxylate groups (COO^-) of PMAA and NH_3^+ of chitosan associated with the formation of nanoparticles. Besides, formation of a new band at 1704.22 cm^{-1} representing the formation of (C=O), which approve the presence of PMAA in the chitosan nanoparticle composition; which is in full agreement with the published report [20].

X-ray diffraction (XRD)

The X-ray diffraction patterns of native chitosan and CNPs were recorded in Fig.4. The diffraction pattern of native chitosan shows two peaks at $2\theta=10^\circ$ and 20° indicating the ordered crystalline structure of chitosan. While, these peaks become weak in the XRD diffraction pattern of chitosan nanoparticles, through the formation of other new peaks at $2\theta = 11.7^\circ$, 16.4° , 18.41° and 22.3° ; which fully agree with the published report [21].

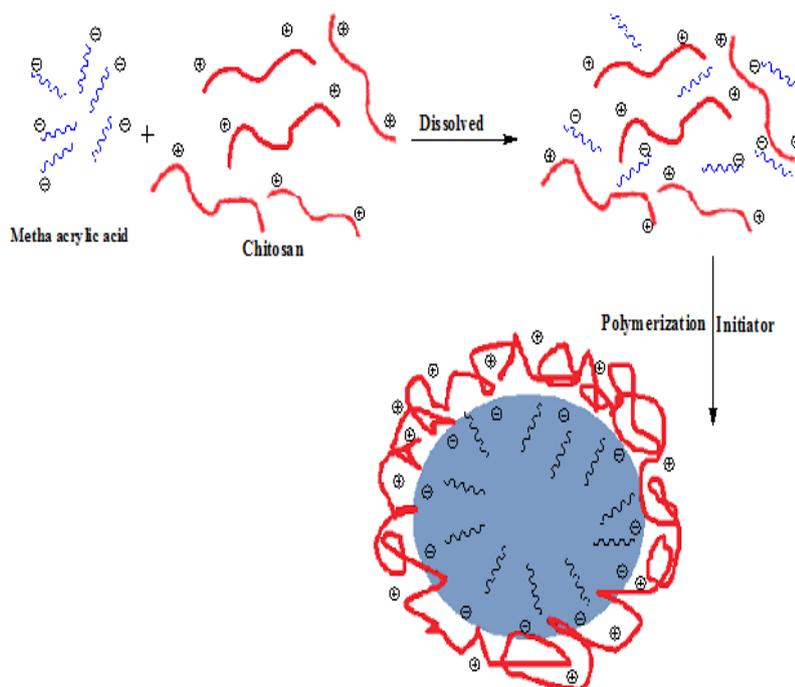


Fig.1. Schematic diagram for fabrication of chitosan–PMAA nanoparticles (CNPs).

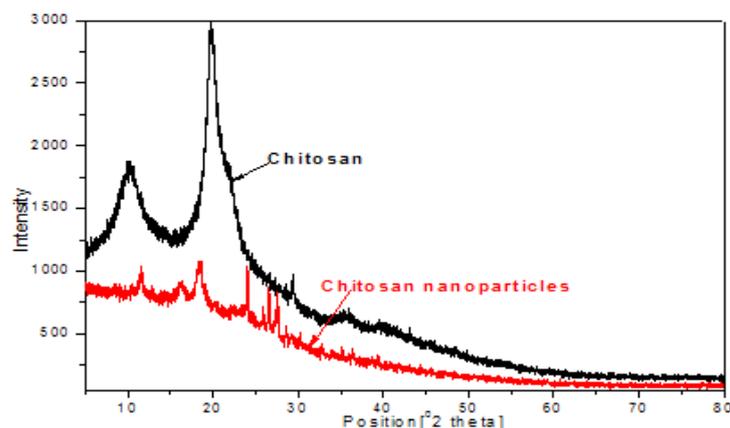


Fig.4. X-ray diffraction patterns of chitosan and chitosan nanoparticles.

Thermo gravimetric analysis (TGA)

TGA analysis is an effective technique to evaluate the thermal stability of the nanoparticles. The TGA thermo grams of native chitosan and CNPs are shown in Fig. 5. Based on the TGA diagram of chitosan and chitosan nanoparticles, the initial weight loss of 14.57% for chitosan and 8.56% for chitosan nanoparticle occurred at 100°C corresponding to the evaporation of intra- and inter-molecular moisture. While, at 200°C, the weight loss of 24.96% for chitosan and 11.96% for chitosan nanoparticle, were observed,

corresponding to the thermal decomposition of functional groups, such as OH on the chitosan backbone. But at 300-500 °C, the weight loss of 56.50%, 69.78% and 81.77% for chitosan and 29.17 %, 46.2% and 55.38 % for chitosan nanoparticle, respectively were observed. This weight loss portion was produced by the thermal decomposition of the chitosan backbone. These results displayed that chitosan nanoparticle are more thermally stable compared with native chitosan.

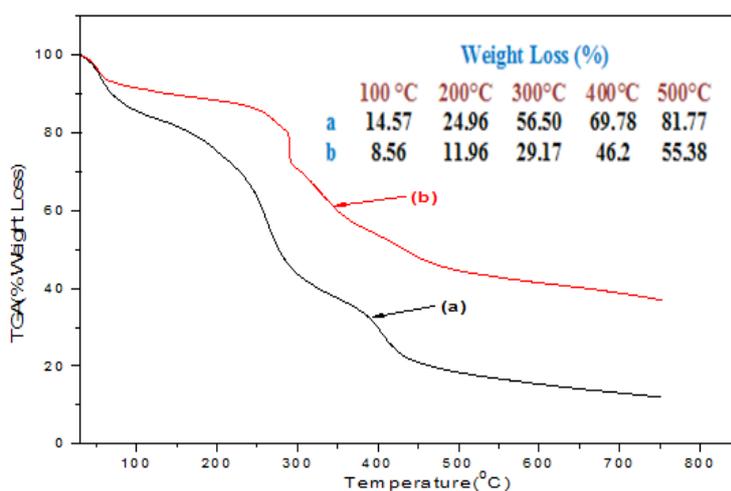


Fig. 5. Thermo gravimetric analysis of (a) chitosan (b) chitosan nanoparticles.

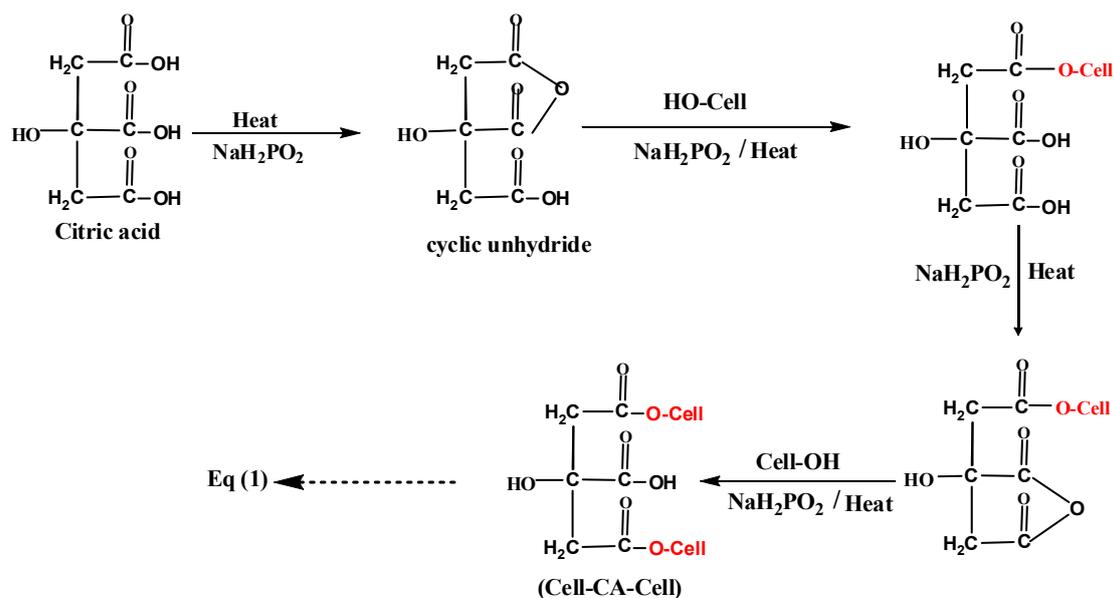
Optimizing the factors affecting the performance of finished cotton fabrics in presence of CNPs

Crosslinking reaction mechanism

When cotton fabric is treated with a citric acid as a non-formaldehyde cross-linking agent and the highly reactive CNPs as an ecofriendly multifunctional finish in presence of sodium hypophosphite as a potential catalyst, the following three main reactions are predictable

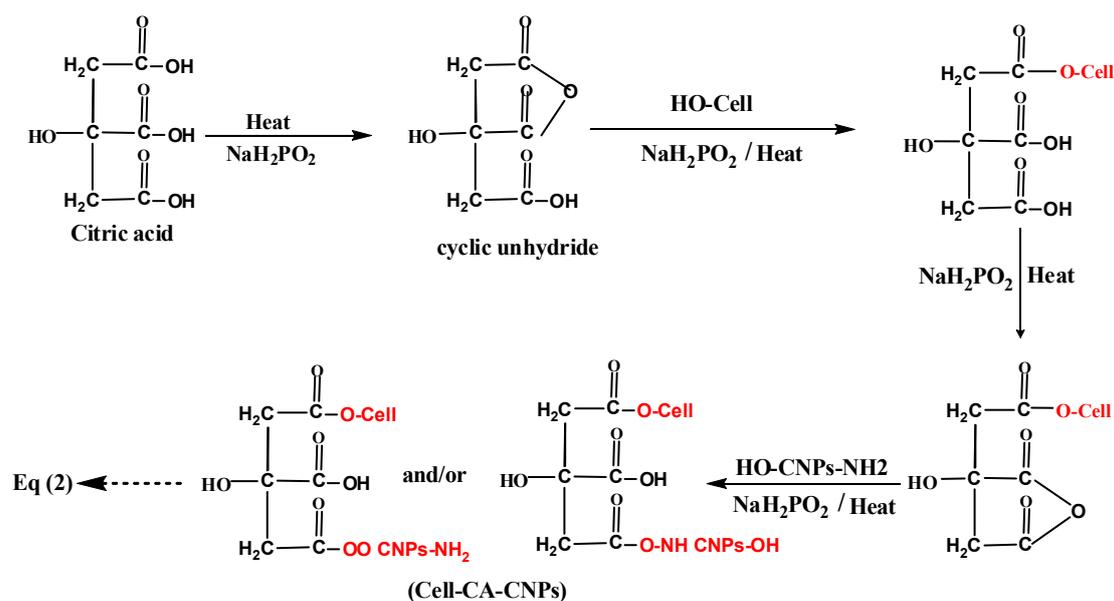
to occur through the following crosslinking mechanism:

Reaction 1: Ester crosslinking between two cellulose molecules and citric acid in presence of NaH_2PO_2 thereby linking two adjacent cellulose chains via esterification reaction, which lead certainly to an enhancement in the WRA and decrease in tensile strength of the finished fabric i.e. (Cell-CA-Cell).



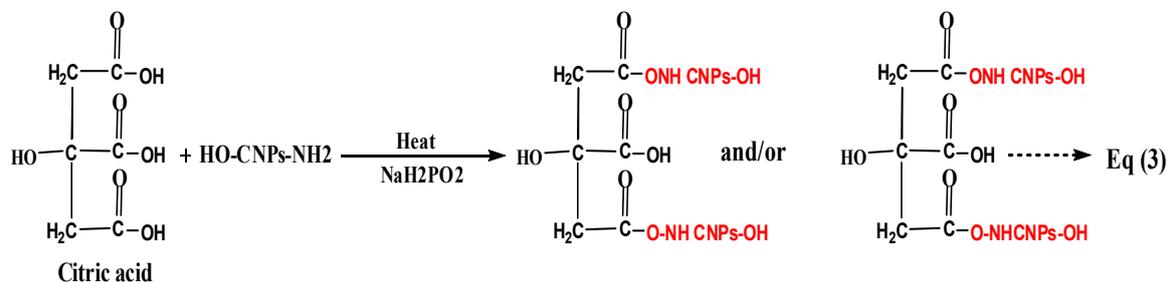
Reaction 2: Crosslinking between cellulose molecules and CNPs molecules with citric acid molecule in presence of NaH_2PO_2 as a bridge between cellulose molecules and CNPs molecules

via esterification reaction, which may also lead to an improvement in the tensile strength of the finished fabrics, i.e. (Cell-CA-CNPs).



Reaction 3: Crosslinking between CNPs molecules with the citric acid bridging two CNPs molecules via esterification reaction, which not employ considerable effect on the

wrinkle recovery angle and tensile strength and removed from the finished fabric after consecutive washing process, *i.e.* (CNPs-CA-CNPs) as shown below.



By taking the above three reactions in mind, the cross-linking agent (*i.e.* CA) is involved in the above three main reactions, thereby affecting its exhaustion. Thus, the extent of formation of such reactions and their impact on the fabric performance with respect to ease and care characteristics and fabric comfort as well as antibacterial properties would be anticipated due to the finishing conditions including citric acid and CNPs concentrations as well as curing time and temperatures. Factors affecting the treatment such as CA and chitosan nanoparticles concentrations as well as temperature and curing time and the onset of this on fabric performance and antimicrobial properties are discussed in the following sections:

Chitosan nanoparticles concentration

Table 1 discloses the discrepancy of nitrogen %, dry wrinkle recovery angle, tensile strength, elongation % at break and stiffness of finished cotton fabrics at different CNPs concentrations ranged from (0–20 g/l). Details of the conditions used are given in the text. It is shown from the table that (a) the wrinkle recovery angles of the finished cotton fabrics decreases by increasing the CNPs concentration and still comparable with that finished in absence of CNPs and, (b) all other fabric performance like tensile strength, elongation % at break and stiffness increases considerably. This can be elucidated as described previously in section 3.3.1. (*i.e.*, reaction 2 prevails over other two reactions). In addition to the obtained results that have been confirmed instrumentally by SEM (Fig. 6), FTIR spectra (Fig. 7) and the obvious steady increase in nitrogen % of chitosan fixed on fabric after finishing during the increase in CNPs concentration as shown in Table 1. For more

elaboration and confirmation, the highly reactive CNPs with smaller particle size (60-100 nm) and larger surface area can easily penetrate inside the bulk of the fabric together with citric acid as an ecofriendly green anchoring finish and reinforce the fabric structure. The latter can be confirmed by our world class facilities, *i.e.* instrumentally by:

Firstly: SEM images of cotton fabrics finished in absence and presence of CNPs (Fig. 6 (b and c) in comparison with unfinished one (Fig. 6 (a)). Besides, the surface of the untreated cotton fabric (Fig. 6 (a)) was designated as a smooth surface and normal spiral ribbon-like structure, while certain swelling and surface roughness appeared on the cotton fabric finished in absence of CNPs due to crosslinking reaction (Fig. 6 (b)). Whereas, cotton fabric finished in presence of CNPs disclosed a certain amount of deposited solid material (dots) and thin coated film with more roughness on its surface (Fig. 6 (c)), probably due to the presence of the CNPs.

Secondly: FTIR spectra for confirming the formation of new ester carbonyl band groups at 1726 cm^{-1} and 1721 cm^{-1} for cotton fabric samples finished in absence and presence of CNPs (Fig. 7 (b and c); *i.e.* carbonyl ($>\text{C}=\text{O}$) stretching vibration of carboxylic acid and ester bonds overlapped on cotton fabrics, which cannot be found in unfinished cotton fabric (Fig. 7 (a)). This is in accordance with the published work [22]. On the other word, FTIR spectroscopy results in Fig. 7 confirmed the esterification reaction onto cellulose; at which citric acid esterified to cotton cellulose by formation of cyclic anhydride intermediate. The peak of the OH stretching in the spectrum of the cotton fabric treated by CNPs (Fig. 7 (a)) becomes more abroad due to

the characteristic peak of NH₂ and OH groups of CNPs. This can prove the booming effect of the CNPs as an ecofriendly multifinishing agent during durable press finishing of cotton textile especially with reinforcement effect on finished cotton fabric which can place them in the anti-crease and easy care category of cotton finishing, besides, the fabric stiffness imply that the multi-finished fabrics retain their comfort.

Citric acid Concentration

Table 2 displays the effect of citric acid

concentration (10–100 g/l) on the dry wrinkle recovery angles, tensile strength, elongation at break and stiffness of cotton fabric finished in presence of CNPs concentration (5 g/l). It is obvious from the table that all fabric performance studied increases by increasing the citric acid concentration and can be comparable with that finished in the absence of it. The tensile strength of cotton fabric begins to decrease at very high concentration of citric acid due to the hydrolytic action of high concentration of finishing agent.

TABLE 1. Effect of chitosan nanoparticles concentration on add on %, dry wrinkle recovery angle, tensile strength, elongation at break and stiffness of finished cotton fabrics.

Chitosan Nano Particles Concentration (g/l)	Nitrogen (%)	DWRA	T.S.(N)	Elongation at break (%)	Fabric Stiffness (cm)
0	0	116.3 ± 1.44	330± 2.44	9.63± 3.22	2.93 ± 3.12
2.5	0.19 ± 1.24	112.5 ± 1.22	336.2 ± 1.88	9.75 ± 3.88	3.10± 2.66
5	0.24 ± 1.68	109.3 ± 2.88	348.2± 2.00	9.27± 3.44	3.62± 1.66
10	0.29 ± 2.22	106.2 ± 3.12	352.3 ± 1.22	9.23 ± 3.66	3.72 ± 2.22
20	0.32 ± 1.88	104.0 ± 3.00	356.2 ± 2.66	9.30 ± 2.88	3.76 ± 3.36

Reaction Conditions:

[Citric acid], 30 g/l; [NaH₂PO₂], 15 g/l; [non-ionic wetting agent], 2g/l; drying, at 85°C for 3 min.; curing time 2 min., curing temperature, 150°C .

Note:

0* cotton fabric finished in absence of CNPs

DWRA of untreated cotton fabric= 66.0

T.S. of untreated cotton fabric = 386.4 N

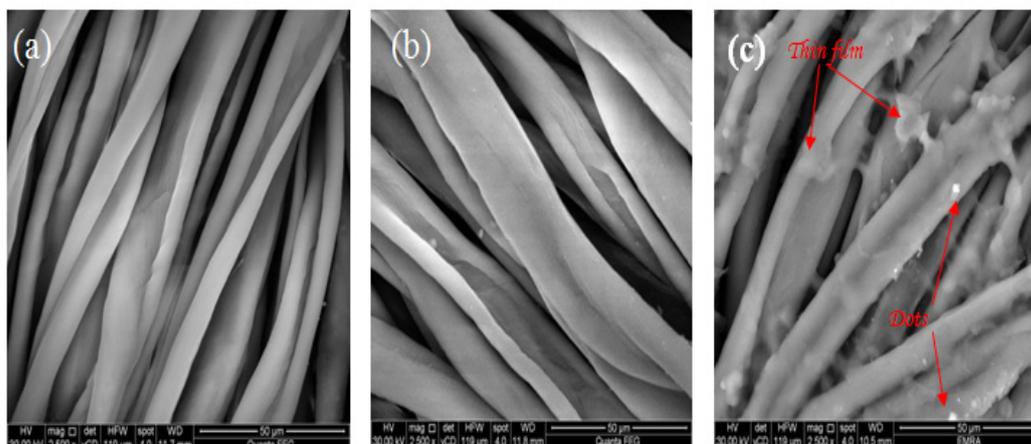


Fig. 6. SEM of (a) un treated cotton fabric (b) cotton fabric finished in absence of chitosan nanoparticles (c) cotton fabric finished in presence of chitosan nanoparticles.

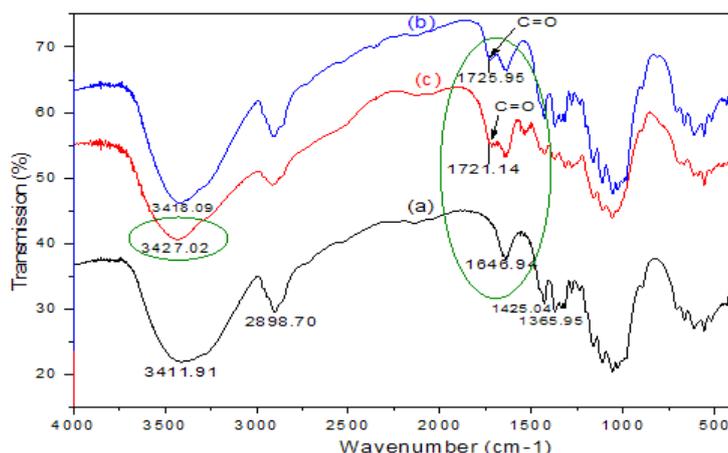


Fig. 7. FT-IR of (a) un finished cotton fabric (b) cotton fabric finished in absence of chitosan nanoparticles (c) cotton fabric sample finished in presence of chitosan nanoparticles.

The above findings can be explicated as shown below:

Firstly: The increment in DWRA of the finished cotton fabric in the presence of CNPs is due to the fact that the reaction 1 prevails over the other two reactions (*i.e.*, 2 and 3); which can be evidenced instrumentally by using FTIR spectra (Fig. 7) and the considerable increase in nitrogen % as shown above in section 3.2.1.

Secondly: The higher tensile strength, elongation at break and stiffness of the finished cotton fabrics in the presence of CNPs than that finished in the absence of it is due to Reaction 2 prevailing over Reaction 1; which can be also confirmed as shown above in SEM image (Fig. 6) as shown above in section 3.2.1.

Curing time and temperature

Table 3 exhibits the effect of curing time and temperature on the dry wrinkle recovery angle, tensile strength, elongation at break and stiffness as well as whiteness and yellowness degree of cotton fabrics treated with cross-linking formulation containing citric acid (30 g/l); NaH_2PO_2 (15 g/l); CNPs (5 g/l); and wetting agent (2 g/l). It is clear from Table III that increasing the curing temperature from 150°C to 190°C and the curing time from 2 min to 4 min is conveyed by an enhancement in the extent of cross-linking reaction (*i.e.* esterification), as proven by the increment in the wrinkle recovery angle and fabric stiffness of the finished cotton fabric and formation of ester carbonyl band at 1726 cm^{-1} using FT-IR spectra. The opposite holds true for tensile strength and elongation at break that is in full agreement with what would be

anticipated. Previous reports [23-25] revealed that tensile strength stands as an inverse function of wrinkle recovery angle. At the same time, tensile strength values of the finished cotton fabrics in the presence of CNPs are higher than that finished in the absence of it, which noticeably reveals the outstanding effect of adding chitosan nanoparticles during durable press finishing of cotton textile as a reinforcing agent of cotton cellulose during the finishing process. On the other hand, It is seen from table III that, unremarkable decrease and increase in whiteness and yellowness degree respectively of finished cotton fabric in absence and presence of CNPs in comparison with unfinished one; may be due to the presence of citric acid as crosslinking agent at higher curing temperatures [26,27]. On the other hand, the degree of whiteness results of cotton fabric finished in presence of CNPs was slightly decreased and degree of yellowness increases considerably. This reflects the role played by CNPs and the net structure formed in the molecular structure of cotton fabric with the latter at higher curing temperatures.

Antibacterial activities

Textile substrates, particularly of natural source, are adequate source for the suitable growth of bacteria as they deliver the circumstances like moisture, temperature, oxygen, and nutrients that are vital for their growth [28]. Cellulosic fabrics, especially cotton is extensively employed in the field of clothing due to their renewability, eco-friendly, hydrophilic properties, air permeability and comfort ability [29]. However, cellulose-based textiles are carriers of micro-organisms and more liable to bacterial attack than synthetic textiles; due

TABLE 2. Effect of Citric Acid Concentration on the dry wrinkle recovery angle, tensile strength, elongation at break and stiffness of finished cotton fabrics.

Citric Acid Concentration (g/l)	DWRA	T.S.(N)	Elongation (%)	Fabric Stiffness (cm)
10	101.3 ± 2.44	319.3 ± 3.22	9.00 ± 1.22	2.93± 2.44
20	105.3± 3.00	336.2 ± 2.88	9.17 ± 3.66	3.10± 3.66
30	109.3 ± 2.88	348.2 ± 2.00	9.27± 3.44	3.62± 1.66
50	113.6 ± 3.88	349.6± 3.46	9.30 ± 3.22	3.72± 2.22
100	115.0± 3.44	343.0± 2.88	9.36 ± 4.00	3.76± 2.66

Reaction Conditions:

[Chitosan nano particles], 5 g/l; [NaH₂PO₂], 50% based on citric acid concentration; [non-ionic wetting agent], 2g/l ; drying, at 85°C for 3 min.; curing time, 2 min., curing temperature, 150°C .

Where;

DWRA of untreated cotton fabric= 66.0

T.S. of untreated cotton fabric = 386.4 N

TABLE 3. Effect of curing time and temperatures on the dry wrinkle recovery angle, tensile strength, elongation at break, fabric stiffness and degree of whiteness of finished cotton fabrics in presence of CNPs.

Temperature (°C)	Curing time (min.)	DWRA	T.S.(N)	Elongation (%)	Fabric Stiffness (cm)	Appearance	
						Degree of Whiteness	Degree of Yellowness
150	2	109.3 ± 2.88	348.2 ± 2.00	9.27± 3.44	3.62 ± 1.66	19.61 ± 1.55	20.61 ± 4.00
	4	111.00± 2.88	334.70± 3.00	9.11 ± 3.22	3.74 ± 2.88	16.70± 3.22	21.03 ± 3.66
	5	114.22± 2.44	330.22± 2.22	9.00 ± 3.00	3.80 ± 3.22	13.98± 2.00	21.93± 4.00
170	2	111.3 ± 2.00	340.2 ± 2.66	9.00± 3.44	3.72 ± 2.22	14.44± 2.88	21.37 ± 3.44
	4	114.6± 3.00	323.70± 3.44	8.88± 3.22	3.94 ± 2.66	12.56± 3.22	22.83 ± 3.12
	5	116.0± 2.66	313.22± 3.22	8.56± 3.00	4.00 ± 3.46	10.16± 4.33	24.13 ± 3.66
190	2	113.3 ± 3.22	330.2 ± 2.00	9.00± 3.44	3.82 ± 3.88	8.47± 4.44	24.18 ± 3.66
	4	116.6 ± 3.00	315.70± 3.88	8.78± 3.22	3.94 ± 3.22	7.16 ± 3.66	26.03 ± 4.00
	5	118.0± 3.44	310.22± 4.00	8.46 ± 3.00	34.12 ± 4.12	6.36 ± 3.88	28.13 ± 3.00

Reaction Conditions:

[Chitosan nanoparticles], 5 g/l; [Citric acid], 30 g/l; [NaH₂PO₂], 15 g/l; [non-ionic wetting agent], 2g/l ; drying, at 85°C for 3 min.

Note:

DWRA of untreated cotton fabric= 66.0

T.S. of untreated cotton fabric = 386.4 N

Degree of whiteness of untreated fabric= 21.93± 2.68

Degree of Yellowness of untreated fabric= 18.68± 2.96

to their properties of porosity, hydrophilic nature along with the ability to maintain water, oxygen, and nutrients, they promote bacterial growth, body odor, and also loss performance properties [30]. By taking the above in mind; recently, numbers of antimicrobial-finished textiles have been recognized for medical perspective to obstruct the spread of pathogens. These products consist of antimicrobial agents such as silver, quaternary ammonium chloride, and chitosan, and showed anti-bacterial activity against a widespread range of microorganisms [31]. Chitosan is one such poly-cationic biopolymer with high antimicrobial activity and possess distinctive properties such as biodegradability, non-toxicity, cationic nature, wound healing and antimicrobial [4]. For all the above advantages, we have used our previously prepared chitosan nanoparticles (60-100 nm) together with CA as a crosslinking agent to produce multi finished cotton fabrics as detailed in the forgoing sections. In this section, the antibacterial activity of these multi finished fabrics is studied under two different methods i.e. quantitative (% reduction) and qualitative (zone inhibition) in addition to their durability to wash. Results obtained and their discussions are given below.

Effect of chitosan nanoparticles concentrations on the antibacterial activities of finished cotton fabrics:

The effect of chitosan nanoparticles concentrations on antibacterial activity of the multi finished cotton fabrics is studied in Table 4. The results designate that the antibacterial

activity is higher as the concentration of chitosan nanoparticles increases irrespective of the test method used. This is attributed to the primary amine groups in chitosan nanoparticles provide positive charges that form ammonium salts which interact with negatively charged residue on the surface of bacteria; such interaction causes extensive changes in the cell surface and cell permeability leading to leakage of intercellular substances. By this way, the growth of bacterial species is hindered and finally leads to the death of these cells. This is in full agreement with the published reports [32-34]. Besides, the mode of antibacterial action of chitosan nanoparticles on bacteria involves binding of the cationic chitosan to the anionic cell surface resulting in changes in permeability. Therefore, it can be said that the effect of chitosan nanoparticles against gram positive bacteria is more dominant than gram negative bacteria most probably due to their differences in the cell wall structure as well as amenability to disruption [35].

Durability to wash for cotton fabric performance finished at optimum conditions:

Table 5 shows the antibacterial activity and easy care characteristics of finished cotton fabrics like dry wrinkle recovery angle, tensile strength, and stiffness after 2, 5 and 10 washing cycles at optimum conditions obtained above. Details of the conditions used are given in the text. It is seen (Table 5) that the amount of chitosan nanoparticles expressed as N%, antibacterial activity, dry wrinkle recovery angle,

TABLE 4. Effect of chitosan nanoparticles concentrations on the antibacterial activities of cotton fabrics finished in presence and absence of CNPs.

Chitosan nanoparticles Concentration (g/l)	Nitrogen (%)	Antimicrobial activity expressed as:			
		(%) Reduction		(Inhibition Zone in mm)	
		<i>S.aureus</i> (G+ve)	<i>E. coli</i> (G-ve)	<i>S.aureus</i> (G+ve)	<i>E. coli</i> (G-ve)
Untreated cotton fabric	0	0	0	0	0
0*	0	10.00	8.44	5.14	3.54
2.5	0.19	70.50	67.35	12.16	10.21
5	0.24	84.45	83.28	15.24	12.37
10	0.29	86.81	85.73	15.93	12.41
20	0.32	90.22	88.20	16.50	13.10

Reaction Conditions:

[Citric acid], 30 g/l; [NaH₂PO₄], 15 g/l; [non-ionic wetting agent], 2g/l ; drying, at 85°C for 3 min. curing time, 2 min.; curing temperature, 150°C.

0* cotton fabric finished in absence of CNPs

tensile strength and stiffness decreases after washing. The multi finished cotton fabric under exploration seems to involve certain amount of unfixed chitosan nanoparticles which are lightly attached to the fabric surface and, therefore, are liable to washing. The latter depends on the number of washing cycles which, in turn, reflects the severity of washing. It is likely that some of the intimately linked chitosan nanoparticles within the cotton fabric is also removed during severe washing; such chitosan removal accounts for the decrement in chitosan content even with the fabric containing the highest amount of fixed chitosan (reaction 3 prevails over the other two reactions) as we mentioned before. Consequently, the treated cotton fabrics with CNPs still maintained better fabric performance after successive washing and still comparable with those finished in absence of it.

Conclusion

Chitosan nanoparticles (CNPs) of size around 60-100 nm as multifunctional ecofriendly finish were prepared from native chitosan by polymerization technique using MAA and potassium permanganate as initiator and fully characterized using SEM, TEM, FTIR and

particle size analyzer. The multifunctional finish is based on the use of chitosan nanoparticles along with the nontoxic citric acid (CA) and sodium hypophosphite as a potential catalyst for such reaction at different curing times and temperatures according to conventional pad-dry-cure method. This was done to see the impact of CNPs on some of technical fabrics performance like dry wrinkle recovery angles, tensile strength, elongation at break, stiffness, degree of whiteness, durability and antibacterial properties; in addition to ascertain the optimum conditions for such esterification reaction. The surface morphology and the reaction mechanism between CNPs and the fabrics were confirmed by FTIR, SEM and nitrogen %. The so obtained fabrics display anti crease and easy care properties in addition to antibacterial properties even after 10 washes. The fabrics retain much of their strength properties and comfort after the multifinishing treatment in question. Finally, our newly prepared freeze drying chitosan nanoparticles introduce an advance in textile finishing processes via introducing ease and care characteristics and antibacterial properties in addition to fabric comfort that basically recommended for using in industrial fabrics of heavy-duty and medical applications.

TABLE 5. Effect of washing cycles on the major technical properties and antimicrobial activity of finished cotton fabrics in presence of CNPs at optimum conditions.

Number of washing cycles	Nitrogen (%)	DRRA	TS (N)	Stiffness (Cm)	Antimicrobial activity expressed as;			
					Reduction (%)		(Inhibition Zone (mm))	
					S.aureus (G+ve)	E. coli (G-ve)	S.aureus (G+ve)	E. coli (G-ve)
0	0.24	109.3	348.2	3.62	83.28	84.45	12.37	15.24
2	0.20	107.5	340.2	3.51	80.51	81.20	10.90	13.80
5	0.15	103.2	336.5	3.20	70.89	72.50	9.98	11.66
10	0.12	100.0	330.0	3.00	60.25	61.12	9.65	10.51

Reaction Conditions:

[chitosan nanoparticles], 5g/l; [Citric acid], 30 g/l; [NaH₂PO₂], 15 g/l; [non-ionic wetting agent], 2g/l; drying, at 85°C for 3 min. curing time, 2 min.; curing temperature, 150°C.

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تخليق وتوصيف جزيئات الكيتوزان النانوية المجففة بالتجميد كمادة تجهيز متعددة الوظائف وصديقه للبيئه لإنتاج منسوجات قطنيه سهله العناية ومضادة للبكتيريا

محمود مرسى، خالد محمد مصطفى، هبة عبدالمجيد أيمن، أمل عبدالحمد البيسى، على محمد صلاح^١ و محمد عادل يوسف^٢

^١المعهد القومى للقياس والمعايرة - الجيزة - مصر و^٢كلية العلوم - جامعة حلوان - القاهرة -مصر

تم نقل الخصائص المضادة للبكتيريا والعناية السهلة للأقمشة القطنية باستخدام مواد تجهيز متعددة الوظائف وصديقه للبيئه تشمل حمض الستريك وجسيمات الكيتوزان النانوية. وقد تم تحضير جسيمات الكيتوزان النانوية من الكيتوزان بحجم فى المدى من ٦٠-١٠٠ نانومتر من خلال البلمرة بحامض الميثاكريليك مع الكيتوزان باستخدام برمنجنات البوتاسيوم كبادئ للتفاعل، مع التوصيف الكامل لتلك الجسيمات باستخدام الميكروسكوب الإلكتروني الماسح و الميكروسكوب الإلكتروني النافذ و مطيافية الأشعة تحت الحمراء و محلل حجم الجسيمات و تحليل الحيود باستخدام الأشعة السينية بالإضافة إلى خاصية التحلل الحرارى. وقد تم دراسة مختلف العوامل المؤثرة على تفاعل التجهيز باستخدام نظام الغمر-التجفيف-التحميص فى وجود جسيمات الكيتوزان فى الحيز النانومتري مثل تركيز الكيتوزان وحامض الستريك وزمن ودرجه حراره التحميص ومدى تأثيرها على أداء النسيج من حيث خواص العناية السهلة والنشاط المضاد للبكتريا وذلك للحصول على انسب الظروف لتفاعل التجهيز. بالإضافة إلى معرفة تأثير تلك الجسيمات النانوية لتحقيق وظائف وخصائص متعددة للأقمشة القطنية المجهزة مثل فقد مقبول فى قوة الشد و الاستطالة عند القطع مع زاويه رجوعيه مناسبه يمكن مقارنتها بمثيلاتها المجهزة بالإضافة إلى زيادة خاصية تصلب النسيج مع قدرة عاليه على تحمل الغسيل بالإضافة إلى النشاط المضاد للبكتيريا باستخدام الطريقه الكميه والكيفيه للبكتريا الموجهه والسالبه. ومن النتائج التى تم التوصل إليها، أظهر التوصيف باستخدام كلا من مطيافية الأشعة تحت الحمراء و الميكروسكوب الإلكتروني الماسح مدى التغير فى التركيب الكيميائي والتركيب السطحي للأقمشة القطنيه قبل وبعد التجهيز في وجود وعدم وجود جسيمات الكيتوزان النانوية. بالإضافة إلى أن هذه الأقمشة أظهرت نشاط مضاد للبكتريا الموجهه والسالبه حتى بعد ١٠ دورات الغسيل. وقد تم دراسته آلية التفاعل بين القطن ومواد التجهيز المستخدمه مثل حمض الستريك و جزيئات الكيتوزان النانويه.