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Super hydrophobic cotton fabrics via green techniques

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ABSTRACT

Nowadays researches interested to prepare super hydrophobic of cotton fabrics without using flour derivatives compound which are harmful to both humans and environments. This research aimed to prepare super hydrophobic cotton surface with dual effect for antibacterial activity through two main processes. First, preparation of (beeswax/chitosan, nano chitosan) emulsion and applied to cotton fabrics Then treated cotton was coated with the prepared Nano silica, which is prepared. Several parameters were studied such as concentration of Bess wax, concentration of chitosan and concentration of nano chitosan. The treated fabrics are characterized by FT-IR, SEM, EDX, TGA, some physical properties such as water permeability, air permeability, tensile strength, roughness, whiteness and contact angle and antibacterial test

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INTRODUCTION

Superhydrophobic materials with water repellent properties receive great attention in the textile industry [1].

Superhydrophobicity is defined as a surface with higher contact angle more than 150° to water which has great industrial and scientific interest due to their relevance in water repellency, friction reduction, self-cleaning and antifouling [2, 3], the superhydrophobic fabrics have low durability to wash and poor abrasion fastness [4].

Cotton have a great number of -OH groups on a surface, which cable of forming hydrogen bonds with water molecules enabling water to spread all over the surface and lead to absorption on it, so it considered as hygroscopic and hydrophilic material by nature which have water contact angle changing between 17° and 47° [5, 6]. Cotton fabrics allow water to spray and absorption on the surface due to the high Roughness of the cotton and capillary action between cotton fibers [7].

The fabrications of super hydrophobic cotton surface depend on increasing the roughening of the low surface energy surface or decreasing surface energy by chemical modification [8, 9].

Due to the presence of -OH groups in cellulose structure, the surface energy of cellulose decreased by reaction of it with different materials through esterification with an anhydride or acid chemicals such as fluorocarbons, silicones, and some organic and inorganic materials. Silicones [10, 11] and organic materials [12-14] are the most popular low surface energy materials. Although fluorocarbons show, the lowest surface energy known but they are rarely found in the organic materials in nature.

Waxes are considered to be the most hydrophobic natural substances due to a high content in tri- di-or monoesters of long-chain fatty alcohols and acids, aldehydes, ketones, di-ketones, sterols, triterpenols and triterpenic acids [15], Long-chain carbon molecules containing one or two hydroxyl groups, Their chemical compositions rely on their sources such as vegetal, animal or mineral origin.

Cotton fabrics were treated with droplets of paraffin and beeswax, Paraffin waxes has exhibited lower contact angles and a low thickness than beeswax on the coated cotton fabrics [16], in another study cotton fabrics are treated different natural substance such as bee's wax, chitosan, propolis high to get antibacterial activity against both gram-positive bacteria Staphylococcus aureus and Streptococcus β haemolytic, and gram-negative bacteria Escherichia coli and Pseudomonas aeruginosin to be used in medical fields. This treatment also improved fabric comfort properties, became less air permissive and more hygroscopic after the treatment [17].

We now turn our attention to methods to produce nano-Roughness which can be created through sol-gel processing, layer-by-layer, colloidal assembly, and electrochemical reaction, and deposition, electrospinning and phase separation.

A new way for the preparation of superhydrophobic surfaces in the textile industry are dependent on the functionalization of SiO_2 nanoparticles with fluorosilicates [18] or non-fluorinated alkylsilanes [19-21] these functionalized SiO_2 nanoparticles has an interesting approach for imparting cotton and polyester fabrics high hydrophobicity property [18].

We committed to develop a simple procedure and low-cost method to prepare the superhydrophobic cotton surface with antimicrobial effect. This study aimed for fabrication of super hydrophobic surface which treated with an emulsion of bee's wax and chitosan followed by nanostructured surface of silicon. The treated fabrics are characterized by FT-IR, SEM, EDX, TGA, some physical properties such as water permeability, air permeability, tensile strength, Roughness, whiteness and contact angle and antibacterial test

MATERIALS AND METHODS

2.1. Materials

Bee's wax (Merck), Chitosan (Alfa Aesar Company, Medium molecular weight, viscosity 1860 cps, the degree of deacetylation 79.0%), penta sodium tripolyphosphate (TPP). Sodium hydroxide (Modern Lab chemicals, Egypt). Methyl alcohol, ethyl alcohol and acetic acid (Sisco Research Laboratories, India), tetra ethyl ortho silicate (Merck), ammonia solution (Alfa Aesar Company) and all other chemicals used are analytical grade and were used without further purification. Two bacterial strains from the bacterial lab, botany department, the faculty of women for art, science & Education, Ain shams university, Cairo, Egypt were employed. They include Staphylococcus aureus (*S. aureus*) as Gram-positive (*G +ve*) bacteria and Escherichia coli (*E. coli*) as Gram-negative (*G -ve*) bacteria. S. aureus and E. coli were selected as test cells because they are the most frequent bacteria in the wound infection and represent Gram positive and Gram negative bacteria, respectively fresh inoculants for antibacterial assessment were prepared in nutrient broth at 37°C for 24 hours.

2.2. Methods

2.2.1 Preparation of chitosan nanoparticles

Chitosan nanoparticles were prepared based on method mentioned elsewhere [22].

2.2.2. Preparation of silica nanoparticle

Silica nanoparticles prepared by alkaline hydrolysis of the tetraethyl orthosilicate followed by the dehydration, condensation reaction [23].

2.2.3 Preparations of bee's wax/chitosan and nano-chitosan emulsion

Bee's wax-chitosan emulsion was prepared by mixing bee's wax solution with chitosan solution at 80 ^{o}C. briefly, Chitosan was dissolved in 1% (v/v) acetic acid and leaving it under stirring for 24 h. and bee's wax was dissolved in methyl alcohol, then add the chitosan solution into bee's wax solution, the mixture solution was homogenized using a high-shear probe mixer for 5 min at 10,000 rpm until completion of homogenization [8, 9]

2.2.4 Treatment of fabrics with bee's wax/ chitosan emulsion/silica nanoparticle

The washed and dried cotton fabrics padded with an emulsion of bee's wax/ chitosan with different concentration of chitosan, Nano chitosan and bee's wax. All samples are immersed in solutions for 1 min. squeezed to 100% wet pickup then padded with the second layer of silica Nanoparticle, all samples dried for 5 min. at 100 °C and curried for 3 min. at 160 °C.

2.3. Characterization

- The prepared samples were performed by a JASCO FT-IR-6100 Fourier transform infrared spectrophotometer using the KBr pellet disk method for transmittance measurements.
- Shape and size of chitosan Nanoparticle was investigated using JEOL, TEM-Speciments for TEM measurements.
- Contact angle of the treated fabrics samples was determined by Compact video microscope (CVM) that is manufactured by SDL-UK, contact angle measured by horizontal plate camera perpendicular to liquid droplet plane.
- The tensile strength of Fabric samples was determined by the ASTM, Test Method D5035. AQ-Test1/5 tensile tester was used.
- Water air permeability was measured by the Toyoseik –japan by standard method ASTMD-583.
- Water air permeability was measured by the Toyoseik -japan by standard method ASTMD-737.
- The surface Roughness was measured by surfacoder 1700a.
- Thermogravimetric analysis was carried out in the central laboratories national center. By using simultaneous thermal gravimetric analyzer (Perkin Elmer thermo-gravimetric analyzer, TGA7, the heating rate is 10 °C/min., USA)
- SEM of the treated fabrics was studied using a scanning electron probe micro analyzer (type JXA 840A)–Japan. Surface morphologies were imaged at different magnifications, using 30kVaccelerating voltage.
- Elements percentages in the adsorbent surface were confirmed by using energy dispersive X-ray photoelectron spectroscopy (EDX) from OXFORD model (INCAX Sight) and supplied with Scanning Electron Microscope JEOL JXA- 840 Electron PROBE micro analyzer microscope

2.4. Assessment of Antibacterial Activity in vitro:

The antibacterial spectrum of antibiotic-loaded chitosan nanoparticle-treated fabrics and antibiotic loaded fabrics were determined against the test bacteria by disk diffusion method on an agar plate [24, 25]. Briefly, 1 cm diameter blended film samples were cut and put into 10 ml of nutrient agar, to which 10ml of microbe culture was inoculated after the solidification. The plates were incubated at 37 °C for 24 hrs. After which the diameter of inhibition zone was measured and recorded.

RESULTS AND DISCUSSION

Under the acidic condition, chitosan was considered to be a good emulsifier to prepare stable chitosan/ bee's wax emulsion, because of the interaction between positively charged chitosan with negatively-charged bee's waxes [26, 27].

There are many factors affecting on the Roughness and the contact angle of the cotton surface which coated chitosan/ bee's wax with emulsion (Emulsion films basically consist of waxes molecules distributed in a chitosan solution) such as the concentration of chitosan, nano-chitosan, and concentration of bee's wax.

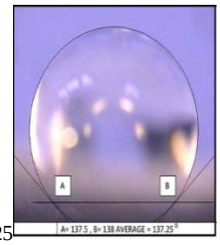
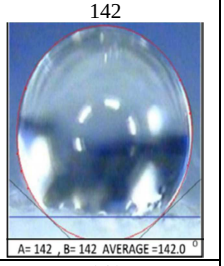
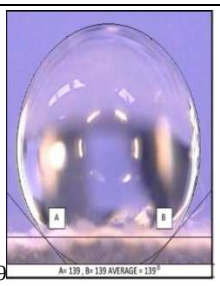
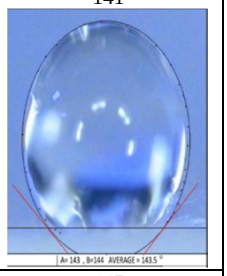
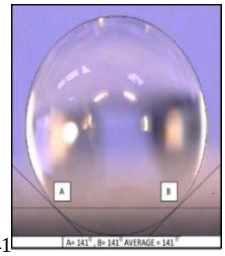
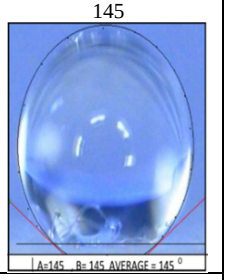
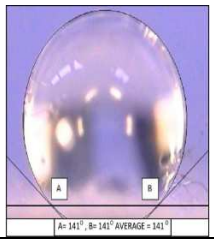
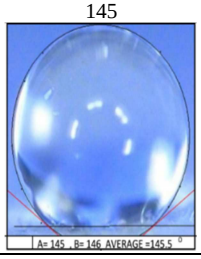
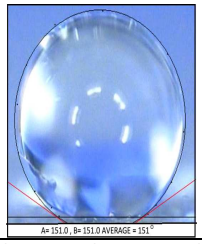
3.1Bee's wax concentration

3.1.1. Effect of bee's concentration on the roughness and the contact angle

The effect of concentration bee's wax was evaluated by measuring the contact angle and the roughness on the treated cotton fabrics at a constant concentration of chitosan (0.5%), nano-chitosan (0.2%).

The cotton fabrics treated with an emulsion of bee's wax (0.5-2%), 0.5% chitosan and 0.2% nano-chitosan as described before. As shown from the table (1).

Table (1): Effect of concentration of bee's wax of chitosan/ bee's wax emulsion on the contact angle and roughness of treated fabrics

Bee's wax Concentration	Chitosan/ bee's wax emulsion		Nano Chitosan/ bee's wax emulsion	
	Roughness Value	Contact angle	Roughness Value	Contact angle
blank	22.06	Zero	22.06	Zero
0.5	18.84	137.25 	16.55	142 
1	18.11	139 	15.82	141 
1.5	17.06	141 	15.42	145 
2	16.21	141 	13.98	145 
2+nano silica	16	151 	13	152 

**Fabrics were dried at 80 °C for 5 min. followed by fixation at 160°C for 3 min.*

From table (1) it is obvious that 2% bee's wax gave the highest contact angle and roughness value due to forming a thin layer at the cotton surface which improve the hydrophobicity of it; the contact angle slightly increases with increasing bee's wax concentration. Also the contact angle increase by adding nano silica layer t as an addition the cotton fabrics from 141 to 151,145 to 152 for each chitosan/ bee's wax, nano-chitosan/ bee's wax emulsions respectively which increase the surface energy of the cotton fabrics.

3.1.2 Effect of bee's wax on antibacterial activity

The Antibacterial properties of cotton coated with chitosan/ bee's wax, nano-chitosan/ bee's wax emulsions are measured against Staphylococcus aureus (*S. aureus*) as gram-positive bacteria and Escherichia coli (*E.coli*) as gram-negative bacteria

Table (2) also shows the antibacterial properties of cotton coated with chitosan (0.5%)/ bee's wax, nano-chitosan (0.2%)/ bee's wax emulsions at different bee's wax concentration.

It is clear that when increasing the concentration of bee's wax from 0.5 to 2% the antibacterial activity of cotton coated with chitosan/ bee's wax, nano-chitosan/ bee's wax emulsions are increased with increasing absorbed dose for both Gram-positive and Gram-negative bacterium. The inhibition zone of gram positive and gram negative for cotton coated with chitosan/ bee's wax, nano-chitosan/bee's wax emulsions increased with increasing the concentration of bee's wax from 0.5-2 %.

Table (2): Effect of bee's wax concentration on antibacterial activity of the cotton treated with chitosan/ bee's wax, nano chitosan/ bee's wax emulsions

Bee's wax concentration %	Chitosan/ bee's wax emulsion		Nano chitosan/ bee's wax	
	+Ve	-Ve	+Ve	-Ve
0.5	0.5	0.5	9	7
1	5.5	4	12	9.5
1.5	15	15	15	13
2	20.5	18	19	18
2+nano silica	22.5	19	20	19

3.1.3 Effect of concentration of bee's wax of chitosan/ bee's wax emulsion on physical and mechanical properties

The changes in some physical and mechanical properties of the cotton fabric treated by chitosan/ bee's wax, Nano chitosan/ bee's wax emulsions were evaluated by monitoring the tensile strength, water permeability, and air permeability.

Table (3, 4) show the tensile strength, water permeability and air permeability of cotton fabrics treated with chitosan/ bee's wax, Nano chitosan/ bee's wax emulsions with different bee's wax concentrations. From table (3) the tensile strength and water permeability were increased with increasing concentration of bee's wax more than blank due to The viscoelastic bee's wax emulsion gives high luster, deeper, high tensile strength and elasticity [28], but the air permeability decrease with increase the bee's wax concentration due to closing of the free zones in the geometry of cotton fabrics [17].

Table (3): Effect of concentration of bee's wax of chitosan/ bee's wax emulsion on the tensile strength, water, and air permeability treated fabrics

Bee's wax Concentration %	Tensile strength	Elongation	Water permeability (sec.)	Air permeability ($cm^3/cm^2.sec$)
Blank	60	15	0.1	95
0.5	61	14	0.148	84.5
1	62	10	0.192	73.66
1.5	63	13	0.249	71.5
2	65	15	0.246	70.5
2+nano silica	65	15	0.255	69

Table (4): Effect of concentration of bee's wax of nano-chitosan/ bee's wax emulsion on the tensile strength, water, and air permeability treated fabrics

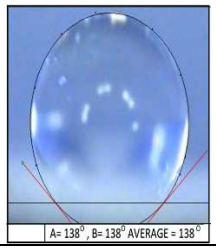
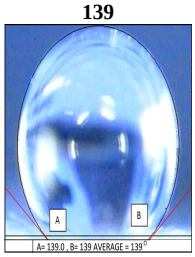
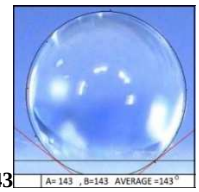
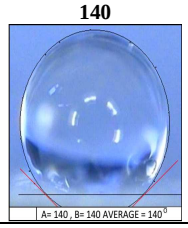
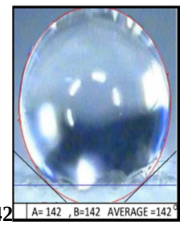
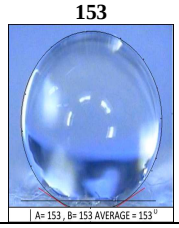
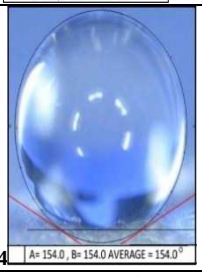
Bee's wax Concentration %	Tensile strength	Elongation	Water permeability (sec.)	Air permeability (cm3/cm2.sec)
Blank	60	15	0.1	95
0.5	63	15	0.192	78.5
1	64	13	0.282	72.8
1.5	64	12	0.310	72.4
2	65	14	0.428	69
2+nano silica	66	13	0.525	62.9

3.2 Effect of chitosan concentration

3.2.1Effect of chitosan concentration on the roughness and the contact angle

The effect of chitosan concentration solution and on Nano chitosan were evaluated by measuring the contact angle and the roughness on the treated cotton fabrics at constant of the concentration of bee's wax 2%, the data are presented in the table (5).

Table (5): Effect of concentration of chitosan in chitosan, nano chitoasn/ bee's wax emulsions on the contact angle and roughness of treated fabrics

Chitosan Concentration	Roughness value	Contact angle	Nano chitosan Concentration	Roughness value	Contact angle
0.5	20.50	138 	0.1	19.25	139 
1	19.25	143 	0.15	18.13	140 
1.5	18.13	142 	0.2	17.96	141 
2	17.96	151 	0.2+ nano silica	17.4	153 
2+ nano silica	17.5	154 			

**Fabrics were dried at 80 °C for 5 min. followed by fixation at 160°C for 3 min.*

From table (5), it is obvious that, 2% concentration of chitosan gave the highest contact angle 151 and roughness value; the contact angle increase with increasing the concentration of chitosan in chitosan/ bee's wax emulsion. Also, the contact angle increase by adding nano silica layer to the treated cotton from 151 to 153 of chitosan/ bee's wax emulsion due to lowering the energy surface but roughness value decrease with increasing the chitosan concentration and the same for nano-chitosan.

3.2.2 Effect of chitosan concentration on antibacterial activity

The Antibacterial properties of cotton coated with chitosan/ bee's wax, nano-chitosan/ bee's wax emulsions are measured against Staphylococcus aureus (*S. aureus*) as Gram-positive bacteria and Escherichia coli (*E.coli*) as gram-negative bacteria

Table (6,7) show the antibacterial properties of cotton coated with chitosan/ bee's wax, nano-chitosan/ bee's wax emulsions at different chitosan concentration and the treated with a layer of prepared nano silica.

Table (6): Effect of chitosan concentration on cotton treated with chitosan/ bee's wax emulsion on antibacterial activity

Chitosan concentration %	Chitosan/ bee's wax emulsion	
	+Ve	-Ve
0.5	16.5	14.5
1	18	16.5
1.5	19	17
2	20	19.5
2+nano silica	21	20

Table (7): Effect of chitosan concentration on cotton treated with nano chitosan/ bee's wax emulsion on antibacterial activity

Chitosan concentration %	Nano chitosan/ bee's wax	
	+Ve	-Ve
0.1	9.5	7
0.15	18	12.5
0.2	18	12.5
0.2+nano silica	19	12.5

Table (6,7) show that when increasing the concentration of chitosan from 0.5 till 2%, 0.1 till 0.2 the antibacterial activity of cotton coated with chitosan/bee's wax, nano-chitosan/bee's wax emulsions are increased with increasing absorbed dose for both gram-positive and gram-negative bacterium. The inhibition zone of gram positive and gram negative for cotton coated with chitosan/bee's wax, nano-chitosan/bee's wax emulsions increased with increasing the concentration of bee's wax from 0.5-2 %. The extra layer of nano silica also gives increasing or constant in zone inhibition in gram +ve and gram –ve as shown from the table (6, 7).

3.2.3 Effect of chitosan concentration of chitosan/ bee's wax, nano-chitosan/ bee's wax emulsion on physical and mechanical properties

The tensile strength, water absorbance, and air permeability are considered physical properties the following discussion clear how the concentration chitosan and nano-chitosan effect on them.

Table (8, 9) show the effect of chitosan and nano-chitosan in bee's wax emulsion, in table (8) when chitosan concentration increasing from (0.1-0.2%) the tensile strength increase due to crosslink between the fiber molecule by various forces between amino (-NH_2) hydroxyl (-OH) groups of chitosan and hydroxyl group of cellulose molecule [17, 29]. For nano-chitosan samples, the small particles of nano-chitosan penetrated inside the fiber molecules and causes more increase in tensile strength. The air permeability and water absorbance for the sample treated with different concentration of chitosan and chitosan nanoparticle decrease due to the porous of fabrics closed by the thin film of chitosan and nano-chitosan/ bee's wax emulsion. All these physical properties were improved by adding a final layer of nano silica as clear from the table (8, 9).

Table (8): Effect of chitosan concentration of nano-chitosan/ bee's wax emulsion on the tensile strength, water, and air permeability treated fabrics

Concentration of nano chitosan	Tensile strength		Water permeability (sec.)	Air permeability (cm3/cm2.sec)
	Tensile strength	Elongation		
Blank	60	15	0.1	90
0.1	**45**	**38**	**0.211**	**76.6**
0.15	**50**	**32**	**0.222**	**75.34**
0.2	**58**	**12**	**0.429**	**70.6**
0.2+ nano silica	60	12	0.532	69.3

Table (9): Effect of chitosan concentration of chitosan/ bee's wax emulsion on the tensile strength, water, and air permeability treated fabrics

Chitosan Concentration	Tensile strength		Water permeability (sec.)	Air permeability (cm^3/cm^2.sec)
	Tensile strength	Elongation		
Blank	60	15	0.1	90
0.5	49	35	0.161	93.05
1	54	12	0.273	80.4
1.5	64	10	0.309	76.6
2	63	11	0.343	73.24
2+ nano silica	65	15	0.425	70

3.3 Characterization of Nano silica

During the sol-gel process, TEOS was first hydrolyzed to silicic acid as shown in figure (1). Then, condensation reactions lead to the formation of Si-O-Si bonds and colloidal silica nanoparticles would appear

$$Si(OC_2H_5) + H_2O \rightleftarrows Si(OH)_4 + 4C_2H_5OH$$

$$2Si(OH)_4 \rightarrow 2(Si - O - Si) + 4H_2O$$

Figure (1): Sol-gel process of silicic acid

3.3.1 TEM of silica Nanoparticle

The TEM picture of silica nanoparticle is shown in figure (2), the average diameter of the nanocomposite silica solution was estimated in range 44 nm to 76 nm. The particles size of the nanocomposite was under 100 nm. The silica nanoparticles are almost in a spherical shape and smooth. However, some particles seem to be larger in size and possess different shapes due to agglomeration phenomenon [30-32].

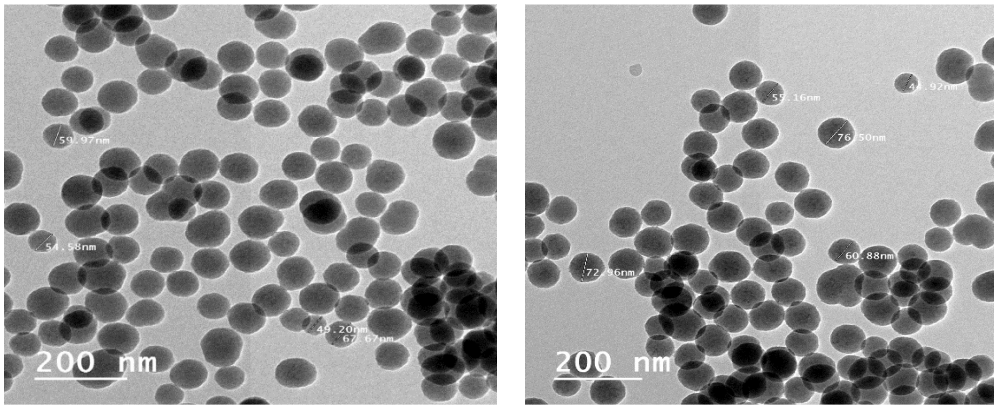


Figure (2): TEM images of nano silica prepared and its nano size range

4.3.3.2 FTIR of silica nanoparticle

The FTIR spectra of the silica nanoparticles are presented in the figure (3). The spectra of Figure (3) exhibited a number of characteristic spectral bands, such as the peaks at 1077 and 454 cm^{-1} due to the asymmetric stretching vibration, symmetric stretching vibration and bending vibration of Si–O–Si, respectively, which are the specific bands of the silica nanoparticles [33-35]. The peak at 937 cm^{-1} is ascribed to the stretching vibration of Si–OH [36].

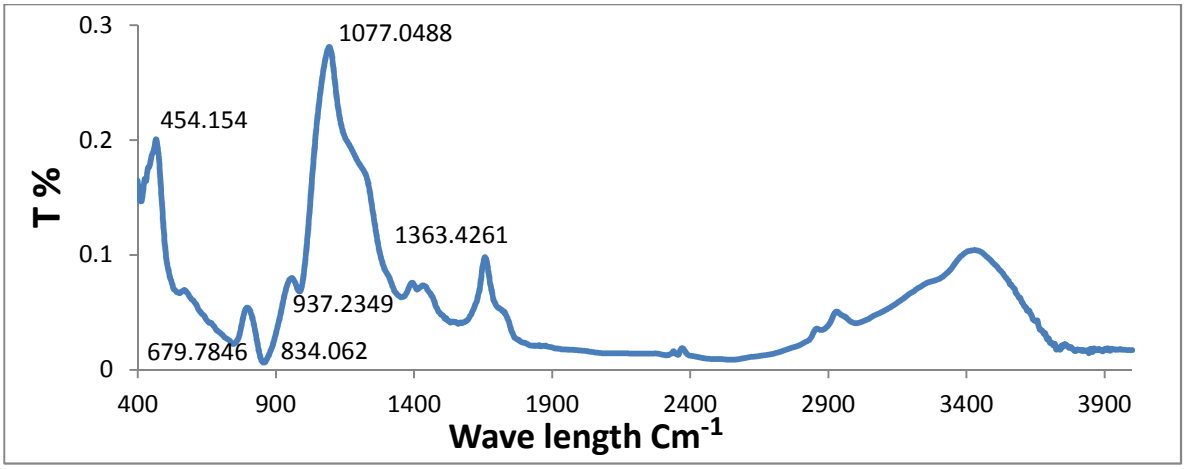


Figure (3): FTIR of silica Nanoparticle

4.3.4 Scanning electron microscope of treated fabrics

Figures 4 (a, b, c &d) show the SEM of (a) control cotton fiber,(b) cotton coated with 2% bee's wax/chitosan emulsion, (c) cotton coated bee's wax/2% chitosan emulsion, (d) cotton coated optimum bee's wax/chitosan emulsion with nano silica, respectively.

SEM technique was used to investigate the surface morphology of the untreated and emulsion treated fabrics, Figure 4(a) reflects smoothness of the cotton blank whereas figure 4(b, c) reflects a rough thin film surface of the bee's wax/ chitosan emulsion without any contaminating particles on their surfaces and closed the fiber distance to each other. Figure 4(d) also shows a high rough layer surface of the bee's wax/ chitosan emulsion with some silica nano particle, which absorbed and precipitin on the cotton surface

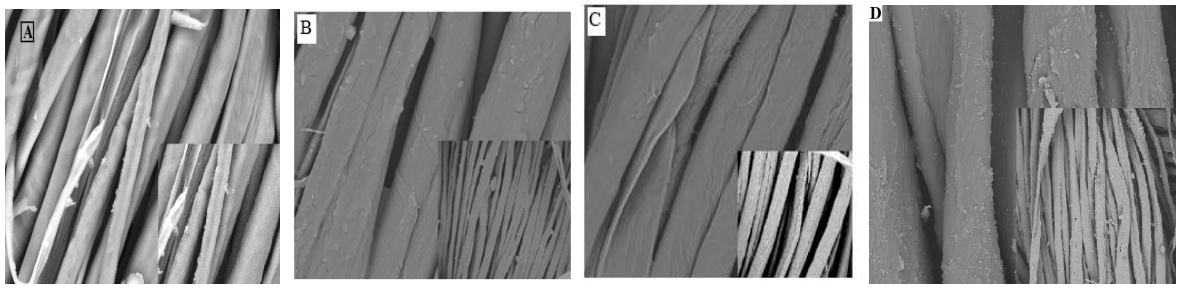


Figure (4): Scanning electron micrographs (x3000, 6000) of (A) control cotton fibre, (B) cotton coated with 2% bee's wax/chitosan emulsion, (C) cotton coated bee's wax/ 2% chitosan emulsion, (D) cotton coated optimum bee's wax/chitosan emulsion with nano silica

Figures 5 (a ,b ,c &d) show the SEM of (a) control cotton fiber, (b) cotton coated with 2% bee's wax/nano-chitosan emulsion, (c) cotton coated bee's wax/0.2 % nano-chitosan emulsion, (d) cotton coated optimum bee's wax/ nano-chitosan emulsion with nano silica, respectively.

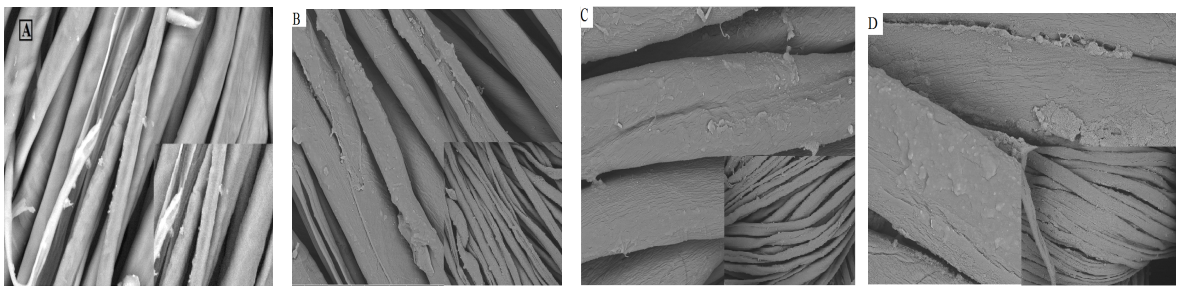


Figure (5): Scanning electron micrographs (x3000, 6000) of (A) control cotton fibre, (B) cotton coated with 2% bee's wax/nano-chitosan emulsion, (C) cotton coated bee's wax/ 0.2% nano-chitosan emulsion, (D) cotton coated optimum 2 % bee's wax/0.2% nano-chitosan emulsion with nano silica

SEM technique was used to investigate the surface morphology of the untreated and emulsion treated fabrics, Figure 5 (a) reflects smoothness of the cotton blank whereas figure 5 (b, c) reflects a homogeneous coating of the bee's

wax/ nano-chitosan emulsion on the entire of cotton fibers which closed the fiber distance to each other. Figure 5(d) also shows completely covered a rough layer of the bee's wax/ chitosan emulsion with some silica nanoparticle which absorbed and precipitin on the cotton surface with uniformly distributed small particles.

4.3.5 Energy-dispersive X-ray spectroscopy

Figures (6, 7) show the Energy-dispersive X-ray spectroscopy of the cotton treated with bee's wax/ chitosan/ nano silica, bee's wax/ nano-chitosan / nano silica emulsion, Energy-dispersive X-ray spectroscopy (EDX) was employed to establish the chemical identity of the observed particles on treated cotton, It can be clearly seen from the EDX analysis (Figure 6, 7) that particles existing on the surfaces of the fibers are silica particle , The presence of the Si signals indicates the successful incorporation of nano-silica in the surface of fibers. The quantity of silica adsorbed on the fabric samples was measured in treated cotton with bee's wax/ chitosan/nano silica, bee's wax/nano-chitosan /nano silica emulsions to be 0.46, 0.06 %, respectively, which agreed with SEM images.

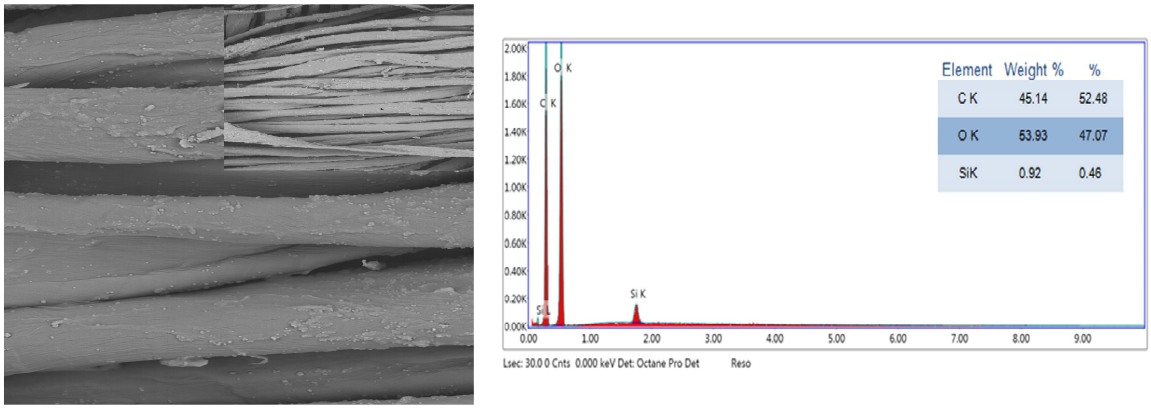


Figure (6): EDX of the cotton treated with bee's wax/ chitosan/ nano silica

3.6 FTIR

Figure (8) show the FTIR of cotton fabric treated with 2% bee's wax/ chitosan emulsion, bee's wax/ 2% chitosan emulsion, 2% bee's wax/ 2% chitosan emulsion/ nano silica as described in preceding method.

Figure (8a) shows the FT-IR spectra of untreated cotton (COT) fabrics show peaks at around 3340, 2900, 1648, 1428 and 1057 cm-1, which are corresponding to the -OH stretching, -CH stretching, -OH of absorbed water from cellulose, -CH_2 symmetric bending and -C–O stretching [37]. The FT-IR of treated cotton fabrics with bee's wax/ chitosan/ nano silica emulsions show the combined bands of COT and chitosan, bees waxes, Nano silica peaks with some shifted peaks in position and intensity due to some physicochemical reactions. In addition, characteristic main peaks of the bees wax appear at 2920, 1460, 1380, 1150 which are corresponding to –CH_2 asymmetric vibration (hydrocarbon), -C=O stretching vibration (esters and fatty acid), -CH_2 vibration deformation (hydrocarbon) and –CH bending vibration (ester), where chitosan main peak at 3440 Cm^{-1} corresponding for –OH and –NH stretching vibration in chitosan molecule, peaks at 2918-2840 Cm^{-1} for –CH stretching and 2247 Cm^{-1} for –CN stretching whereas peak at 1460, 1626 and 1738 for –CO, -C-C and –CH stretching respectively in cotton fabric. The peak which appears at 1057 Cm^{-1} for Si-O-Si stretching in nano silica particle.

Figure (9) also clear the FTIR of cotton fabric treated with 2% bee's wax/ nano-chitosan emulsion, bee's wax/ 0.2 % nano-chitosan emulsion, 2% bee's wax/ 0.2 % nano-chitosan emulsion/ nano silica, the same discussion of the peaks but the sample treated with nano-chitosan appear high absorbance than one treated with chitosan.

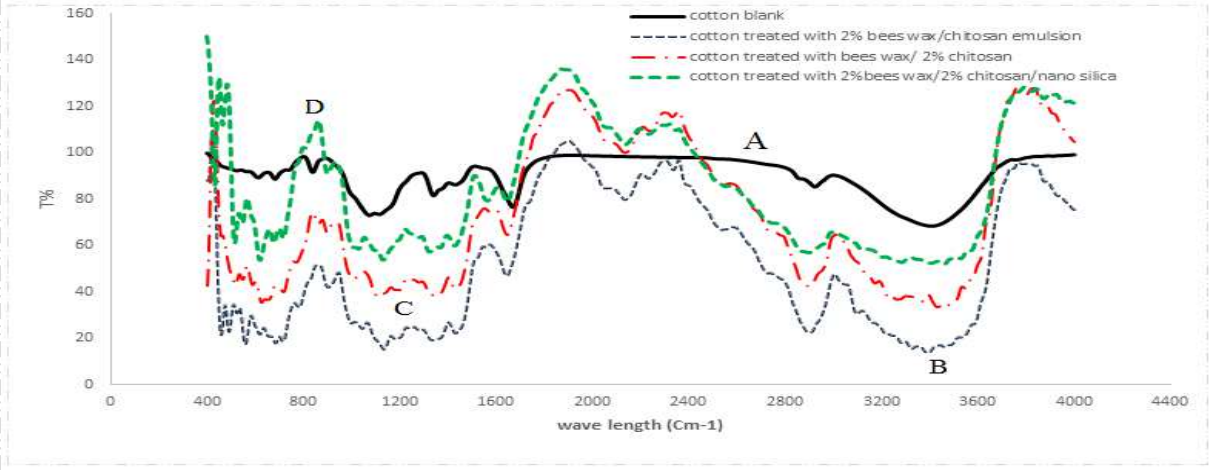


Figure (7): FTIR of (a) untreated cotton, (b) cotton fabric treated with 2% bee's wax/ chitosan emulsion, (c) cotton fabric treated with bee's wax/ 2% chitosan emulsion, and (d) cotton fabric treated with 2% bee's wax/ 2% chitosan emulsion/ nano silica

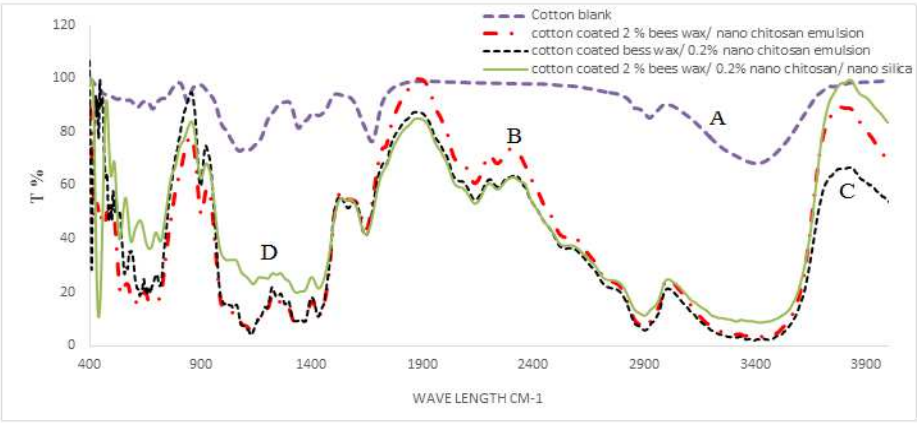


Figure (8): FTIR of (a) untreated cotton, (b) cotton fabric treated with 2% bee's wax/ nano chitosan emulsion, (c) cotton fabric treated with bee's wax/0.2 % nano chitosan emulsion, and (d) cotton fabric treated with 2% bee's wax/ 0.2% nano chitosan emulsion/ nano silica

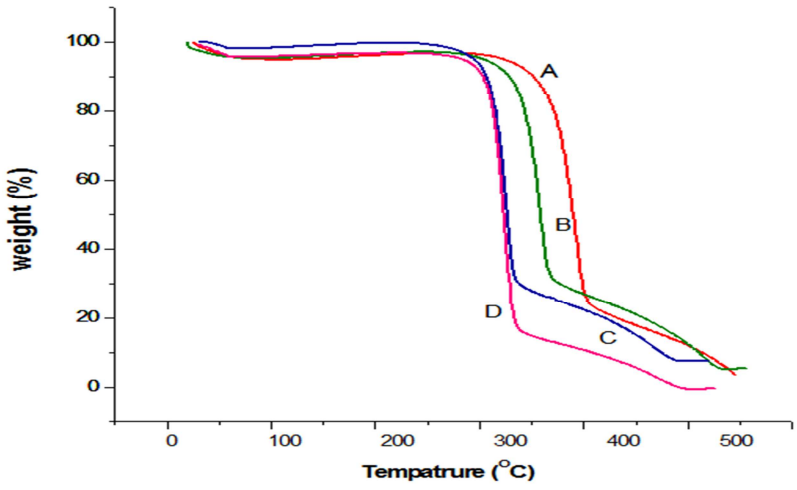


Figure (9): TGA for: (a) Cotton blank, (b) Cotton treated with 2% bee's wax/chitosan emulsion; (c) Cotton treated with bee's wax/2% chitosan emulsion; (d)) Cotton treated with 2% bee's wax/2% chitosan/ nano silica emulsion

4.3.7 Thermal gravimetric analysis

Thermal Gravimetric analysis (TGA) used to describe the change of weight loss with rising temperature. (as small as a decrease of few milligram) can be determined as the sample is heated from room temperature to a certain specific temperature. Thermal behavior of untreated and treated the cotton fabric with Cotton treated with 2% bee's wax/chitosan emulsion; Cotton treated with bee's wax/2% chitosan emulsion; Cotton treated with 2% bee's wax/2%

chitosan/ nano silica emulsion as shown in figure (10). It is clear that there are three main decomposition stages. It is clear that there are three main degradation stages. The first stage represents dehydration, volatilization of few molecular weight substances. The second stage is the main degradation stage and the third stage is the carbonization stage.

The first stage is decomposition stage which below 320 °C due to changes of some physical properties and volatilization of few molecular weight substances. The second stage is the main degradation stage occurs in the temperature range 320-380 °C, the weight loss is very fast due to produce L-glucose and the third stage is the carbonization stage at over 400 °C.

Figure (10) illustrates that the first decomposition temperature of untreated cotton fabric was 330°C, 310°C for Cotton treated with 2% bee's wax/chitosan emulsion, 290 °C for Cotton treated with bee's wax/2% chitosan emulsion and 292 °C for Cotton treated with 2% bee's wax/2% chitosan/ nano silica which cannot show any thermal stability as expected. It is clear that treatment of cotton fabric with Cotton treated with 2% bee's wax/chitosan emulsion; Cotton treated with bee's wax/2% chitosan emulsion; Cotton treated with 2% bee's wax/2% chitosan/ nano silica emulsion show decreases in the decomposition temperature.

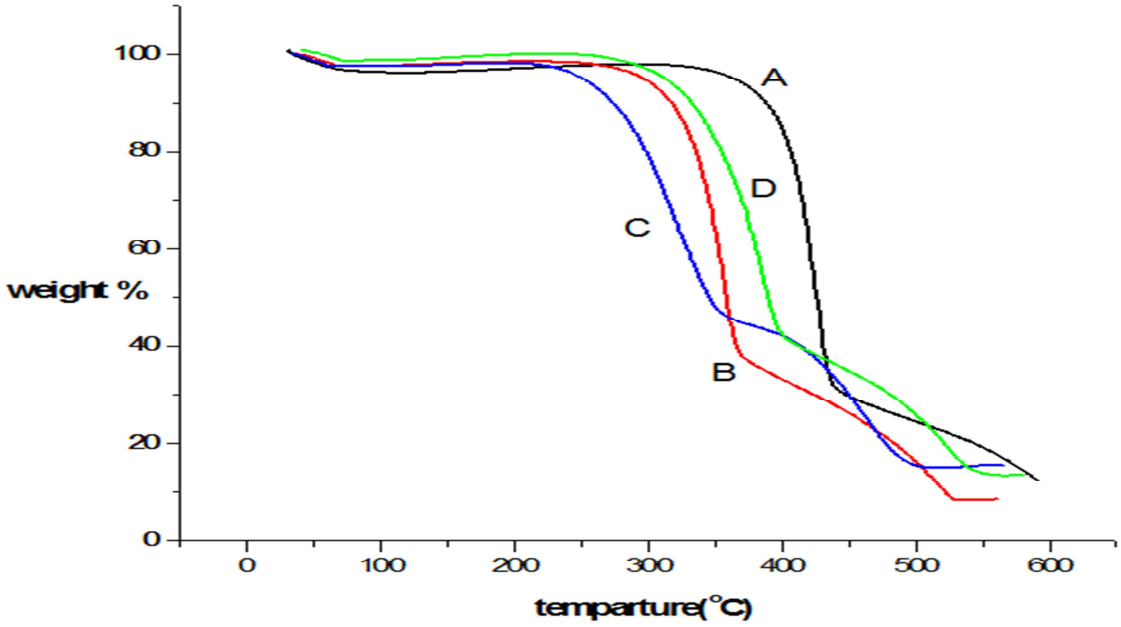


Figure (10): TGA for: (a) Cotton blank, (b) Cotton treated with 2% bee's wax/nano chitosan emulsion; (c) Cotton treated with bee's wax/0.2% chitosan emulsion; (d) Cotton treated with 2% bee's wax/0.2% nano chitosan/ nano silica emulsion

Figure (11) illustrates that the first decomposition temperature of untreated cotton fabric was 330°C, 300°C for Cotton treated with 2% bee's wax/nano chitosan emulsion, 305 °C for Cotton treated with bee's wax/0.2 % nano chitosan emulsion and 292 °C for Cotton treated with 2% bee's wax/0.2% nano chitosan/ nano silica which cannot be show any thermal stability as expected. It is clear that treatment of cotton fabric with Cotton treated with 2% bee's wax/nano chitosan emulsion; Cotton treated with bee's wax/0.2% nano chitosan emulsion; Cotton treated with 2% bee's wax/0.2% nano chitosan/nano silica emulsion show decreases in the decomposition temperature.

CONCLUSION

Development of super hydrophobic of cotton fabrics without using flour derivatives compound was the aim of this research. This research aimed to prepare super hydrophobic cotton surface with dual effect for antibacterial activity through two main processes. First, preparation of (beeswax/chitosan, nano chitosan) emulsion and applied to cotton fabrics Then treated cotton was coated with the prepared silica nanoparticles, which is prepared. The optimum treatment conditions were realized when the fabrics were treated with 2% chitosan, 0.2% chitosan nanoparticles and 2% beeswax emulsion using pad dry cure technique and finally concentration of nano silica 2% which applied on the cotton fabrics as a final layer. The prepared nano silica particles will investigated by TEM and the average diameter ranging from 44-76nm. Whereas the treated cotton fabrics show the best contact angle (154, 151) of chitosan, nano chitosan/beeswax and silica emulsions respectively with improvement in the physicochemical and mechanical of treated cotton fabrics.

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