Antimicrobial and Dyeing Studies of Treated Cotton Fabrics by Prepared Chitosan-PAMAM Dendrimer/Ag Nano-emulsion

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Abstract: In this study, chitosan-PAMAM dendrimer hybrid (ChD) was synthesized through the reaction of chitosan with poly(amidoamine) (PAMAM) dendrimer (Generation -0.5), and characterized by FTIR, SEM, and DSC analyses. In the following, ChD nano-emulsion (ChDN) was prepared by ionic gelation mechanism and finally silver loaded chitosan-dendrimer nano-emulsion (Ag-ChDN) was synthesized. The average particle sizes of ChDN and Ag-ChDN were 265 and 278 nm, respectively. Additionally, the prepared nano-emulsions were applied to the cotton fabric with pad-dry-cure method, and the treated cotton fabrics were characterized by SEM and X-ray diffraction. Antibacterial activity of the treated fabrics against gram negative bacteria (*Escherichia coli*) was evaluated and the results pointed out nano-emulsions had better antibacterial activity in comparison with chitosan. In addition, dyeing ability of the treated fabric was enhanced, and ChDN and Ag-ChDN can be used to diminish salt in reactive dyeing on the cotton fabric.

Keywords: Chitosan, Dendrimer, Cotton, Nano-emulsion, Antibacterial, Dyeing

Introduction

Traditionally, in order to increase the dyeing ability of the cotton with reactive dyes, a large quantity (30-150 g/*l*) of salt was utilized to overcome the static repulsion between the dye molecule and the cotton, therefore highly concentrated salt discharges cause a serious environmental hazard [1]. Therefore, the application of new ecofriendly dyeing method such as salt-free or low-salt dyeing technology in the cotton dyeing with reactive dyes has attracted much attention. The most researchers suggested that the introduction of cationic agents like amine or ammonium into cotton fabrics can reduce or eliminate salt concentration in the dyeing process with reactive dyes [2-4]. The diverse types of chemicals for modification of the cotton have been reported, but most materials have highly toxic and non-biodegradable nature [5]. While the natural base materials such as chitosan show no disadvantages mentioned above, and these materials have attracted the attention of researchers and green labeled manufacturers [6].

Chitosan is produced by deacetylation of chitin, which originates from the outer cover of crustacean like shrimps and crabs [7-10]. Unlike many synthesized polymers, chitosan has remarkable properties like biodegradation and biocompatibility, and compounds produced from the degradation of chitosan are non-toxic, non-allergic, and non-carcinogenic [11-13]. In light of the above, chitosan has various applications in several industries such as pharmaceutical, cosmetics and toiletries, agriculture, textiles with anti-bacterial properties, food, and chemical industries [14-18].

Chitosan modifications have been carried out using multifunctional macromolecules such as crown ethers,

cyclodextrin, and dendrimers to enhance the antibacterial activity of chitosan [19,20]. Dendrimers as a monodisperse polymer with three-dimensional spherical morphology and recognized biocompatible materials are ideal guest-molecule carriers [21,22], which have utilized for modifying chitosan [23,24]. In general, dendrimers are synthesized using either a divergent method or convergent method, and the reactivity and solubility of the dendrimers are determined by the nature of the outer functional groups. Due to their exceptional chemical and physical characteristics, they have also found various applications in biotechnology [25], textile [24,26], and wastewater treatment [27].

Lately, most researchers are considering the possible applications of nanotechnology for generating more attractive and high performance value-added textile materials. Surface modification of textiles with nanomaterials is the newest technique for production of highly active textile surfaces with a range of functionality. Thus in addition to chitosan based antimicrobial textiles where chitosan has been used as a coating or finishing agent [28], synthesis of chitosan nanoparticle has been considered. Researchers reported improvement of antibacterial activity of chitosan in nanoparticle form on polyester fabrics against *S.aureus* [29]. Also, the application of chitosan nanoparticle with different size and zeta potential depending on its molecular weight on wool fabric was studied, and the effect of chitosan nanoparticle concentration on shrink-proof and antibacterial properties of the wool fabric was evaluated [30]. Chitosan nanoparticle dispersion solution was applied to the silk fabric [31], the surface of the chitosan-nanoparticle-treated silk fiber was rougher than that of the chitosan-treated and untreated ones, and a higher specific surface was achieved. Also antibacterial activity, breaking strength, and wrinkle-resistance properties of chitosan-nanoparticle treated silk fabric were also enhanced.

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In addition, there are many reported on chitosan nanoparticles in drug delivery or gene therapy application [32,33].

Silver is an accepted antimicrobial agent with a broad range of activity. But, absorption of silver nanoparticles on textile materials has been challenged due to its low charge density. It was reported that the synthesis of chitosan nanoparticles loaded with silver ion could also be effective against a wide range of microbes with sustained release of silver ion over time [29,34]. Also silver loaded chitosan nanoparticle could be easily absorbed into the textile material accompanied by chitosan nanoparticles without the need of the capping agents [29,34].

The aim of this study is the investigation of dyeing and antimicrobial properties of cotton fabric treated by synthesized ChDN and silver loaded ChDN. For this respect, PAMAM dendrimer (G=-0.5) was used to increase chelating properties of chitosan and then ChDN was prepared using sodium tripolyphosphate (TPP) for the first time. Then, silver ion was added to ChDN and its chelation with silver ions was formed. The prepared nano-emulsions were applied to cotton fabric and antibacterial property of the treated cotton was evaluated. XRD and SEM results were used to identify the modification of cotton fabric. In addition, dyeing and fastness properties of treated cotton fabrics were studied, and an easy way to salt-free dyeing was offered.

Experimental

Materials and Techniques

Chitosan (viscosity 6500 cps, degree of deacetylation (DD) 98 %, molecular weight (MW)>600 kD) was purchased from Chitin India (Mahtani Chitosan PVT. Ltd.). Desized, scoured, and bleached plain-weave cotton fabric (140 g/m^2) was used as received from Mazandran Textile (Iran). Remazol Black B (RBB) and Remazol Red RB (RRR) were supplied by Dystar. Sodium tripolyphosphate was purchased from Merck (Germany). Nonionic detergent (Lotensol, Hansa) was used for fabrics scouring. All the other reagents were analytical grade and used without further purification.

FTIR spectra were recorded on a Nicolet Nexus 670 instrument using KBr pellets under standard operating conditions in the range of 400-4000 cm^{-1}. The measurements were performed at 20 ^{o}C and a relative humidity of 65 %. Zeta Sizer ZEN 3600 Malvern, England was used to identify the particle size of the prepared emulsions. Scanning electron microscope, Seron AIS 2300 was used to characterize the surface properties of synthesized ChD hybrid and modified cotton fabrics. All the samples were coated with gold before SEM testing. Reflective spectrophotometer, Gretag Macbeth Color-Eye 7000A was used to determine the reflection of the dyed fabric at 360-750 nm. XRD studies were performed using a Siemens D5000 X-ray diffractometer (Cu K$_\alpha$, 1.5418 Å, operation voltage 40 kV), to evaluate changes of the treated fabrics. The tear strength of the modified and untreated
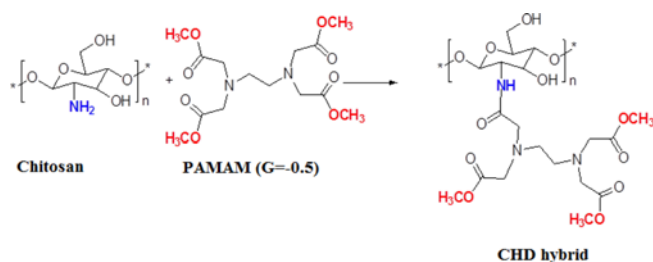
Scheme 1. Preparation of chitosan-PAMAM dendrimer hybrid.

cotton fabric was tested according to BS-2576 by an Instron 5566 tearing instrument. Differential scanning colorimetry (DSC) measurements were carried out by a TA instrument 2010 at a heating rate of 10 ^{o}C/min under the nitrogen atmosphere.

Preparation of ChD, ChDN, and Ag-ChD Nano-emulsions

PAMAM dendrimer (G=-0.5) was prepared by the reagent excess manner starting from ethylene diamine according to divergent procedure offered by researchers [35]. Chitosan was dispersed in methanol, PAMAM (G=-0.5) was added to the prepared suspension and the mixture stirred at 40 ^{o}C for 3 days. Then, the mixture was filtered, and dried at room temperature to give ChD hybrid. Preparation of ChD hybrid is illustrated in Scheme 1.

ChDN was prepared through ionic gelation mechanism with TPP. For this respect, ChD was dissolved in acetic acid (1 % v/v), and the pH of the solution was adjusted to 5 with sodium hydroxide (2 % w/v). Then, TPP in ratio of ChD to TPP, 3:1, was added slowly to ChD solution at 25 ºC.

Silver nitrate (10 mM) was added to ChDN, and stirred for 1 h. Then, the emulsion was centrifuged at 5000 rpm for 30 min. Extra solution was removed, and the remaining was dispersed in distilled water.

Modification of Cotton Fabric

The cotton fabric (2 g) used in this study was washed at the laboratory with nonionic detergent (1 g/*l*), L.R. 40:1 at 60 ^{o}C for 30 min. The fabrics were then dried at ambient conditions. The cotton fabric was immersed into 0.2 % (w/v) of ChD, ChDN, and Ag-ChD nano-emulsions twice with a substrate and liquor ratio of 1:20 for 5 min/each time with a pressing step giving a pick-up of about 90 % after each soaking. Then, cotton fabrics were dried at 80 ^{o}C for 5 min, and cured at 110 ºC for 3 min. After the finishing, fabrics were washed thoroughly with water, and dried at room temperatures.

Determining Antibacterial Property

Antibacterial activity of chitosan, ChDN, and Ag-ChDN treated cotton fabrics was determined according to AATCC 100 standard with *E.coli*. In summary samples (1×1 cm^2) were put into tubes and were autoclaved at 121 ºC for

15 min. Bacteria suspension on nourishing environment (BHI agar) was prepared. 100 μl of bacteria suspension containing 10^6 bacteria was added into tubes (under laminar hood and aseptic condition). Tubes were closed and kept at 37 ºC for 20 h. Then, 10 ml of normal saline was added into tubes so that bacteria were separated from the fabric by normal saline. Successive dilutions of bacteria in every sample were prepared by normal saline. 100 μl of every dilution was incubated in Muller Hinton Agar and petri dishes were kept at 37 ºC for 18 h. Then to obtain the number of bacteria, the number of colonies was counted and multiplied by dilution constant.

Antibacterial effect was determined in order to equation (1):

$$Antibacterial\ effect\ (\%) = \frac{blank-test}{blank} \times 100 \qquad (1)$$

where blank is the number of bacteria on cotton fabric and test is the number of bacteria on treated cotton fabrics with chitosan and nano-emulsions.

Dyeing Procedures

Dyeing was carried out to evaluate dyeing ability of the raw cotton fabric and treated cotton with nano-emulsions. Dyeing of the treated cotton fabric was carried out with RBB and RRR. The modified cotton fabric was introduced in an aqueous bath containing 3 % owf dye at a liquor ratio of 40:1 without adding salt. The temperature was kept at 40 ºC. After 30 min, temperature was slowly raised to 60 ºC (1 ºC/min), and dyeing was continued for 60 min. Then, fixation was conducted for 30 min using sodium carbonate (20 g/l) at 60 ºC. At the end, the dyed fabric was soaped at 90 ºC for 5 min at liquor ratio of 30:1, and then thoroughly rinsed with water.

Conventional dyeing on the untreated cotton fabric was followed the methods suggested by the dye manufacturer in the presence of sodium chloride (25 and 50 g/l) and sodium carbonate (20 g/l) for dye fixation. Finally, washing and rinsing of dyed cotton fabrics were completed according to the method used for the treated cotton fabric.

Color Yield Analysis

The color yield or the color strength expressed as K/S value was calculated from the Kubelka-Munk equation (equation (2)):

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (2)$$

where K is the absorbance coefficient, S is the scattering coefficient, and R is the reflectance ratio measured at the maximum absorbance using a reflective spectrophotometer. After folding each fabric twice, measurements were taken at four different positions on the fabric surface. L^* defines lightness; a^* denotes the red/green value; and b^* is the yellow/blue value, h and c (hue and chromaticity) were calculated

from the reflectance data.

Color Fastness

The washing fastness was evaluated in accordance to the standard ISO 105 C06 C2S:1994 (E) method. The washing was conducted at 60 ºC for 30 min, rinsed with cold water, air dried, and analyzed by grey scales (1-severe staining, 5-no staining). The light fastness test ISO 105 B02:1988 (E) was tested with the xenon arc lamp using blue reference samples. Light fading was assessed on a scale of 1 (severe fading) to 8 (no fading). The rubbing fastness test was performed using a crockmeter in accord with ISO 105-X12:1993 (E). The staining on the white testing cloth was assessed according to the grey scale.

Results and Discussion

Characterization of ChD Hybrid
FTIR Analysis

The FTIR spectra of pure chitosan and ChD hybrid are illustrated in Figure 1(a). The FTIR spectrum of ChD hybrid revealed new absorptions, which were characteristic of PAMAM dendrimer. The FTIR spectrum of chitosan indicated large and intense peak at 3100-3500 cm^{-1} corresponding to the stretching hydrogen bond O-H overlapped with the several N-H stretching bonds. The characteristic absorption peak appeared at 1550-1640 cm^{-1} is attributed to the amide bond. Stretching vibration peaks of C-H appeared at 2850-3000 cm^{-1} and bending vibration peaks of C-H were observed at 1375-1450 cm^{-1}. Symmetric and asymmetric stretching vibration peaks of ether bond in glucopyranose ring were at 1024 cm^{-1}, 1065 cm^{-1}, 1150 cm^{-1} [36]. On the FTIR spectrum of ChD hybrid, in comparison with chitosan FTIR spectrum, the absorption peak at 3443 cm^{-1} was shifted to 3431 cm^{-1} and converted narrower than chitosan spectrum, and relative intensities of the absorbance of C-H bond at 2875 cm^{-1} and 2923 cm^{-1} increased, which was caused by the reaction between -NH$_2$ groups in chitosan and terminal carbonyl groups of PAMAM dendrimer. In addition, a strong absorption peak around 1727 cm^{-1} was observed, attributed to the C=O stretching of ester in ChD hybrid, which was characteristic of PAMAM dendrimer. The FTIR results well confirmed that the reaction between chitosan and PAMAM dendrimer was completed chemically.

SEM Analysis

SEM is the best known and most widely used tool for morphological analyses [26]. Figure 1(b) shows different magnifications of pure chitosan and ChD hybrid. The morphologic changes of chitosan after modification can be clearly observed from these images. Chitosan modified with PAMAM dendrimer clearly showed the presence of variable amounts of foreign deposited materials on their surfaces. Based on the SEM results, it was reasonable to assume that the presence of these deposits might be responsible for the
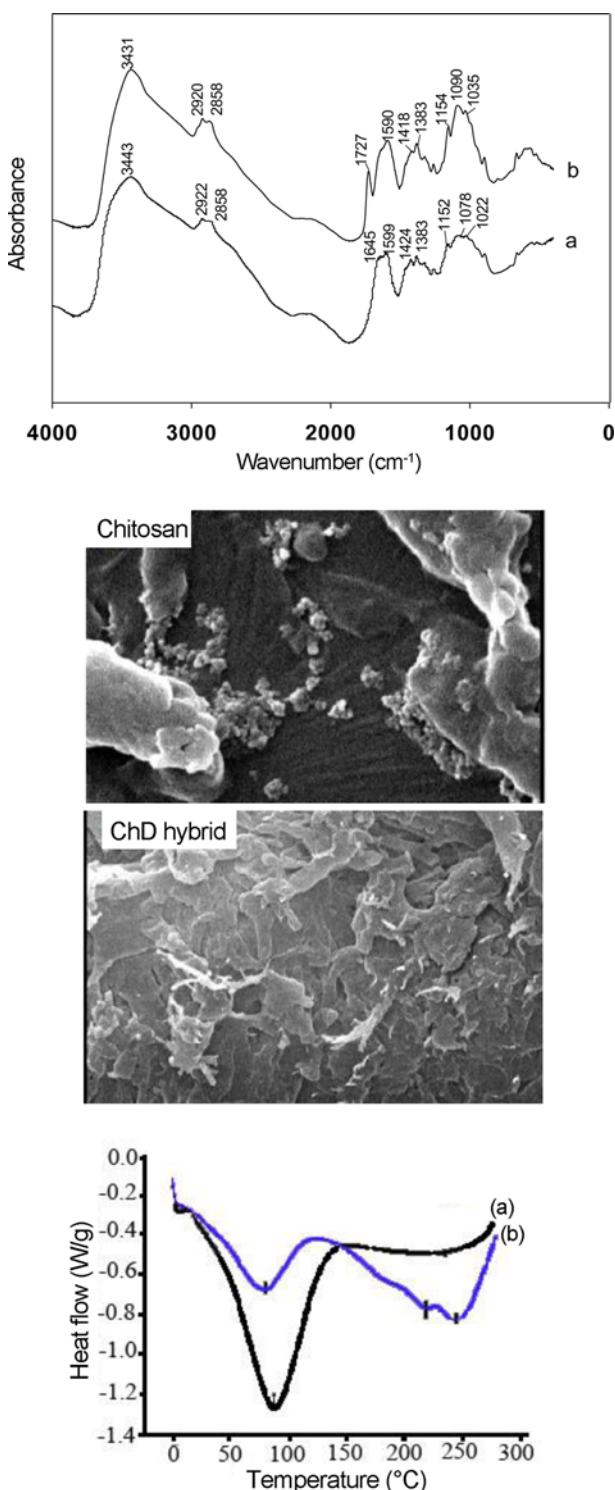
Figure 1. FTIR spectrum, SEM images, and DSC analysis of (a) chitosan and (b) ChD hybrid.

variation of chitosan property.

DSC Analysis

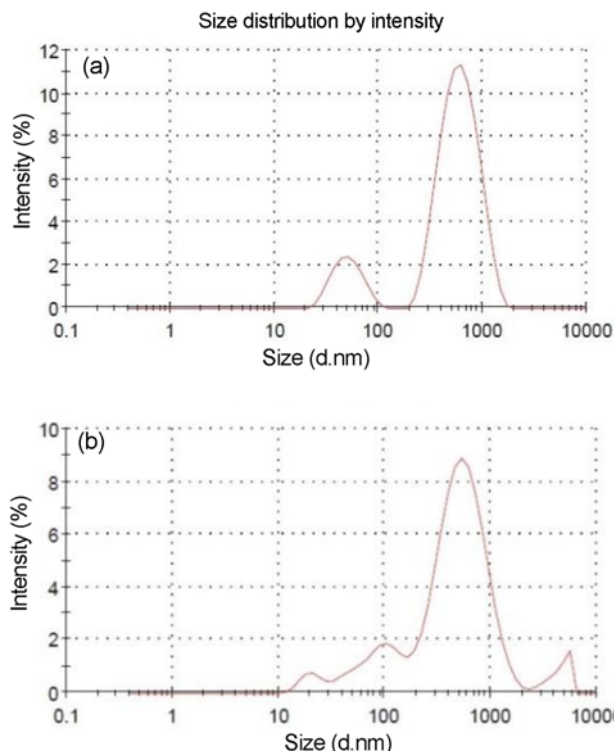Thermal properties of pure chitosan and ChD hybrid were

Figure 2. Size distribution of (a) ChDN and (b) ChD/Ag nano-emulsion.

studied by DSC. In DSC curves (shown in Figure 1(c)), the first peak of chitosan polymer at 60-130 $^{\circ}$C exhibits endothermic peak attributed to the evaporation of absorbed and bound water. For ChD hybrid the initial endothermic peak is due to the loss of bound water. Differences in the peak area and the position of the first endothermic peaks clearly reveal the different water holding capacity of these macromolecules and different water-polymer interaction strength. Degradation of chitosan starts at around 260 $^{\circ}$C. One prominent exothermic peak at around 260 $^{\circ}$C with beginning temperature of 224 $^{\circ}$C and peak temperature of 254 $^{\circ}$C is observed only for ChD hybrid. This is probably due to the cleavage of the interaction between chitosan and dendrimer [29,37].

Characterization of Nano-emulsions

Preparation of nano-emulsions was completed through ionic gelation method using TPP. In this study, ChD solution in different concentrations (1 and 2 mg/m*l*) at pH=5 was used for preparation of nano-emulsions. Different concentrations of TPP were added to ChD solution (ratio of ChD to TPP 3/1). The stable opalescent suspension including nanoparticles was formed in concentration of TPP (1 mg/m*l*) and ChD solution (2 mg/m*l*) [31,37,38]. The size distribution of ChDN is shown in Figure 2(a), and mean particle size of prepared nano-emulsion is 265.6 nm, and the peak occurred in the particle size distribution, signifying excellent uniformity.

Figure 2(b) shows size distribution of Ag-ChD nano-

emulsion. It is clear that size distribution and Z-average of Ag-ChD nanoparticles were increased (278 nm).

Chitosan is very suitable for the adsorption of Ag ions, and the adsorption of ions into chitosan is based on ionic exchange, intracellular trapping, and complex physical adsorption by van der Waal forces [40]. Chitosan nanoparticles are formed via interacting positively charged chitosan and negatively charged tripolyphosphate. The process alters the structure and the electrical surface charge of chitosan due to disrupting the secondary structure forming in its natural one [41]. The high surface area of nanoparticles can provide more sites to bind to metal ions. Therefore, chitosan nanoparticles adsorb Ag ions mainly as ion-exchange resins and surface chelation. Active Ag ions can also dissociate among the porous nanoparticles. Consequently, properties of Ag-loaded nano-particles are significantly against chitosan nanoparticles without Ag [29]. So, the size, surface charge, and morphology of ChD nanoparticles were all affected by loading of Ag ions. Also, it seems that available pores in ChD nanoparticles can be considered as enough bulky sites to adsorb Ag ions. So that, Ag ion first adsorbs onto the external surface of ChD and then bind to ChD nanoparticles. Finally, the ions can be chelated to the internal surface of ChDN. The relatively loose structure of ChD nanoparticles and lower crystallinity in comparison with chitosan allow Ag ions to interact more with pair electrons of ChDN nanoparticles.

Assessments of Cotton Surface Characteristics
SEM Analysis

SEM was used to study the structure and morphology of cotton fabrics after the modification process. The SEM images are shown in Figure 3, and different magnifications (20.00k x, 4.00k x) were used to explore the surface properties of cotton fabrics. The alteration in morphology between raw and treated cotton is further supported by the difference in their SEM images. Figure 3 indicated that the surface of untreated cotton fabric was relatively smooth and appeared as a layered structure, but the morphology of the cotton fabrics modified with nano-emulsions was rougher than the untreated cotton fabric. SEM images clearly showed that nanoparticles form a regular layer on the surface of cotton fiber, and suggesting that nano-emulsions were grafted onto the surface of cotton fabric.

XRD Analysis

X-ray diffraction has been used to evaluate the crystallinity form of the untreated and treated cotton fabric. The XRD
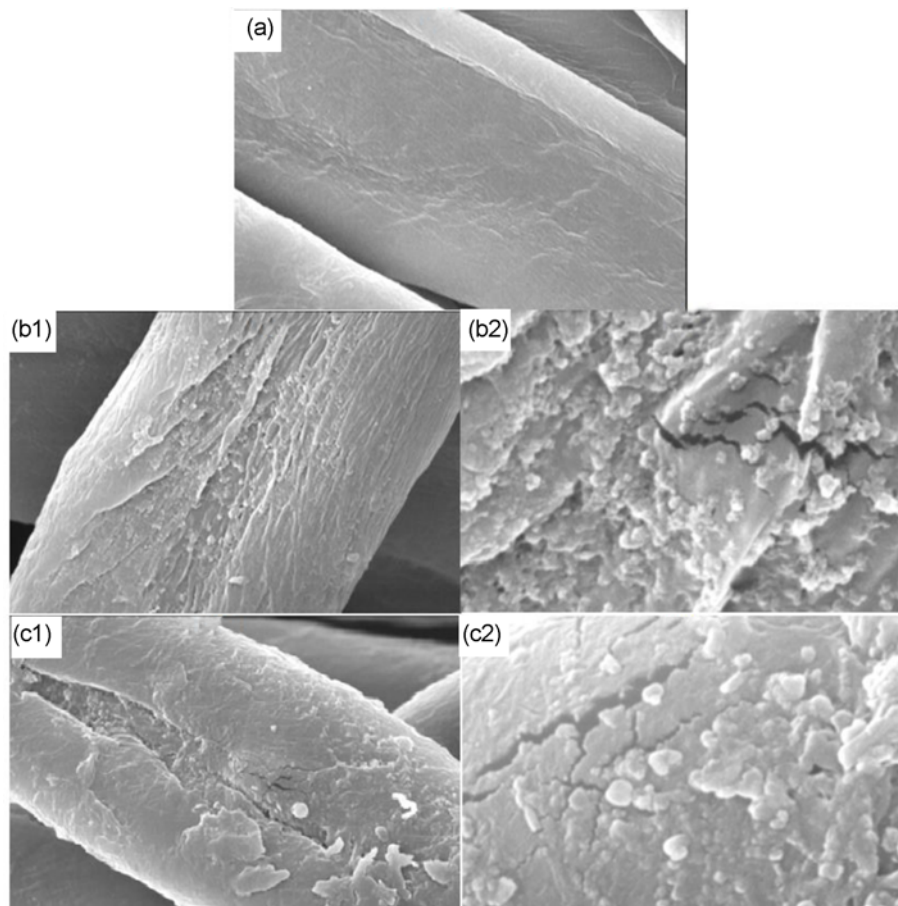

Figure 3. SEM images of (a) raw cotton, (b) cotton fabric treated with ChDN, and (c) cotton fabric treated with ChD/Ag nano-emulsion.
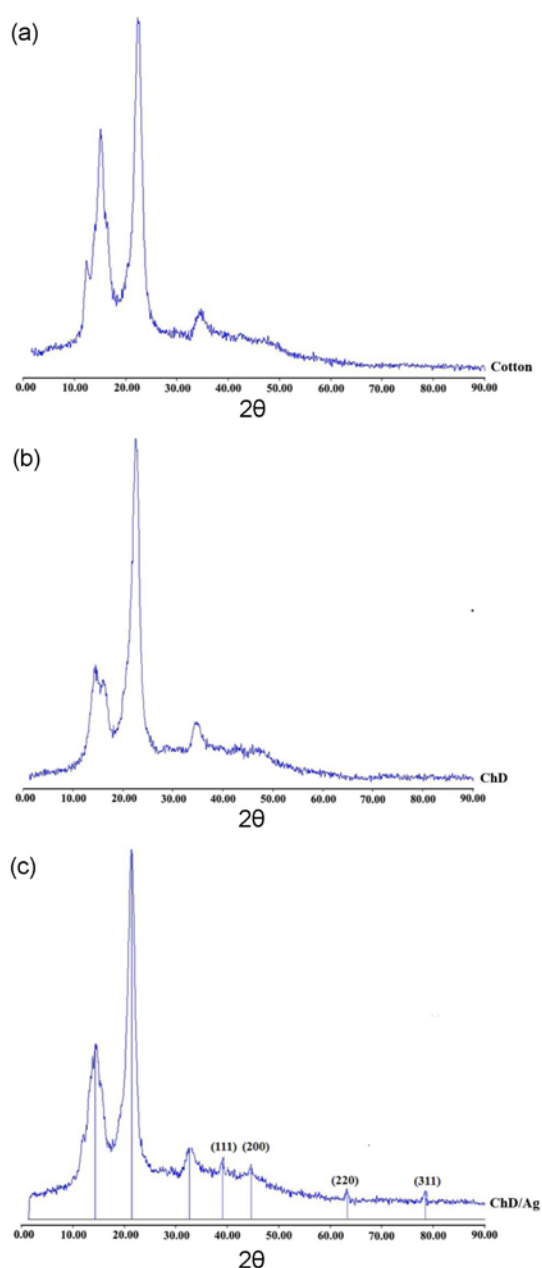
Figure 4. XRD curves of (a) raw cotton, (b) cotton fabric treated with ChDN, and (c) cotton fabric treated with ChD/Ag nano-emulsion.
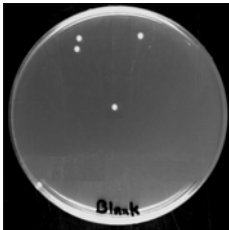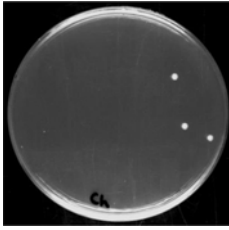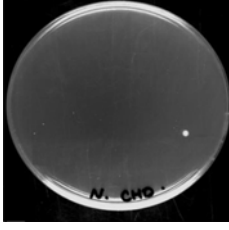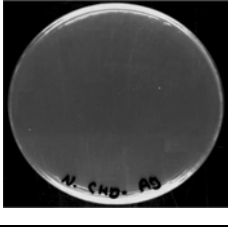
spectrums of the prepared nanoparticles on cotton fabrics are given in Figure 4. It can be seen that the untreated cotton has three characteristic peaks of cellulose I at $2\theta=15°$ (($1\bar{1}0$) plane), $16.5°$ (shoulder, (110) plane), and $22.5°$ ((200) plane) [37]. These characteristic peaks also appear in the XRD patterns of the modified cotton. This result confirms that the position of the major diffraction peaks does not change regardless of the modification process. Indeed, the modified cotton fabrics retained the crystalline structure of

unmodified cotton fabric. Moreover, the crystallinity of the cotton fabric modified with ChDN (30.92 %) and Ag loaded ChDN (32.32 %) decreased compared with the unmodified cotton fabric (34.82 %) without change in crystalline sizes of samples. ChD and Ag loaded ChD nanoparticles on the cotton were not identified clearly. However, the presence of the diffraction peaks at 38°, 44°, 64°, and 77°, which are attributed to the (111), (200), (220), and (311) planes of silver respectively, could confirm that loaded silver was crystallized into a cubic structure, were confirmed [42].

Antimicrobial Activity of Cotton Fabric

The antibacterial activity of the treated fabric has been evaluated quantitatively by AATCC-100 test method. It is clear from Table 1 that both chitosan and ChDN treated cotton indicate higher rate of bacterial reduction as compared to the untreated cotton. But ChDN treated cotton shows even more antibacterial activity than chitosan treated fabric

Table 1. Antimicrobial activity of cotton fabric

Samples	Antibacterial test images	Reduction (%)	Inhibition zone (mm)
Cotton		-	-
Treated by chitosan		25	1.25
Treated by ChDN		75	3.77
Treated by Ag-ChDN		100	5.24

because of the special character of the nano size of ChD particles and their enhanced surface area with higher number of available free amino groups to interact with the bacterial cell surface. The negatively charged surface of cell membrane is the target site of the polycationic ChDN. Therefore, nanoparticles with higher surface charge density interact with the bacteria more than chitosan. ChDN provides higher affinity with bacterial cells for their quantum-size effect. These nanoparticles could be tightly adsorbed onto the surface of the bacteria to disrupt the membrane because of the larger surface area, and cause to leakage of intracellular components and destruction of bacteria cells [11,41]. In addition, PAMAM dendrimer could potentially enhance the antimicrobial performance of chitosan because PAMAM dendrimer can also chelate with essential nutrient of microorganisms and improve the antimicrobial activity of chitosan [24].

Table 1 shows the antimicrobial property of cotton fabrics treated with Ag-loaded ChDN is better than untreated one. The cotton fabrics treated with ChDN and Ag-loaded ChDN cause death of *E.coli* bacteria 75 % and 100 %, respectively. It was found that Ag-loaded ChDN showed higher antibacterial activity than chitosan, and slightly higher than ChDN. The higher surface charge density of Ag-loaded ChDN enhances the affinity with the negatively charged bacterial membrane, and is probably responsible for their higher antibacterial activity. Also, Ag-loaded chitosan nanoparticles could provide controlled release of Ag ions that are dissociated in the small pores of ChD nanoparticles to show continuous antibacterial activity. These results also prove that Ag-ChD nanoparticles may have a dual mechanism of silver and chitosan-dendrimer nanoparticles [29].

The diameters of inhibition zone in the agar plate are given in mm. The tests were replicated three times for each treated samples and the results are presented in Table 1. The Ag-ChD modified cotton textiles placed on the bacteria-inoculated surfaces killed all the bacteria under and around them. A distinct inhibition zone with an average width of 5.24 mm around the cotton samples was observed. The presence of the most inhibition zone of Ag-ChD in comparison with ChD and ChDN clearly indicates that the mechanism of the biocidal action of the cotton fabric is due to the leached Ag ion.

Dyeing Properties

To determine whether the modification of the cotton fabric with prepared nano-emulsions would have enhanced dyeing ability of reactive dyes, the cotton fabric was dyed with two reactive dyes in the presence of salt in concentrations of 25 and 50 g/*l*, but treated cotton fabrics were also dyed in the absence of salt in the dyeing process. According to Table 2, the *K/S* of the treated cotton fabrics was much higher than those of untreated ones. Also, *K/S* values of the treated cotton are similar to cotton fabric dyed at salt concentration 25 g/*l*. The results obviously show the significance of using salt for the normal dyeing of reactive dyes. These results indicated that the positively charge of prepared nano-emulsions caused dyeing ability to increase and less salt was used to dye the cotton with reactive dyes. Thus, low-salt dyeing with reactive dyes was possible for cotton fabrics treated with prepared nano-emulsions.

Fastness Properties

The changes in shade and staining on cotton and nylon were investigated visually with grey scale (Table 3). The washing fastness of the dyed treated cotton was good. Change of shade and staining of adjacent fabrics, both being assessed higher or equal to the values obtained by untreated

Table 3. Color fastness of cotton fabrics dyed with reactive dyes at standard depth (1/1)

Sample	Fastness			
	Rubbing		Washing	Light
	Dry	Wet		
Cotton (salt 25 g/*l*)	5	4-5	5	4-5
Treated by ChDN	4-5	4-5	5	4-5
Treated by Ag-ChDN	4-5	4-5	5	4-5

Table 2. CIELab values of cotton fabrics dyed with reactive dyes

Dye	Sample	a^*	b^*	L^*	c	h	K/S
	Cotton (without salt)	-0.78	-13.06	22.5	13.08	89.66	12.5
	Cotton (salt 25 g/*l*)	-3.16	-14.44	23.7	14.78	77.66	20.0
RBB	Cotton (salt 50 g/*l*)	-2.59	-13.54	21.7	13.79	79.17	23.0
	Treated by ChDN	-0.66	-12.50	20.8	12.52	86.70	21.9
	Treated by Ag-ChDN	-2.00	-12.91	22.8	13.06	81.19	19.4
	Cotton (without salt)	50.49	-2.27	47.3	50.54	-2.57	7.1
	Cotton (salt 25 g/*l*)	52.27	3.39	39.2	52.37	3.71	17.2
RRR	Cotton (salt 50 g/*l*)	53.24	4.75	37.2	53.45	5.05	19.1
	Treated by ChDN	53.70	4.34	37.2	53.88	4.62	18.1
	Treated by Ag-ChDN	52.18	3.85	38.8	52.32	4.22	18.8

Table 4. Evaluation of physical properties of raw and treated cotton fabrics

Direction	Sample	Maximum load (N)	Tensile strain (%)	Tensile stress (MPa)	Modulus (gf/tex)
Warp	Cotton	350	6	175	636634
	Finished by ChDN	359	9	179	94940
	Finished by Ag-ChDN	352	10	177	71918
Weft	Cotton	246	21	123	12473
	Finished by ChDN	289	24	134	9668
	Finished by Ag-ChDN	293	23	149	12360

cotton in the conventional dyeing. Dry and wet rub fastness of reactive dyes on treated fabrics was also comparable with conventional dyeing. Besides, optical stability of the treated fabrics showed satisfactory results compared to that in conventional dyeing. Results clearly showed that pretreatment with nano-emulsions had no adverse effect on the fastness properties of reactive dyes.

Physical Properties of Treated Fabric

Table 4 shows data of physical properties of cotton fabric and treated cotton fabric with nano-emulsions at 25 °C and 48 % relative humidity. To assure the accuracy of data, at least three individual measurements were preformed, averaged, and reported. The reproducibility of all reported data was acceptable, with standard deviation ≤4 %. The results showed nano-emulsions altered the elastic properties of the cotton fabric. Such differences were mainly related to reacting cotton with nano-emulsions, and this causes the fabric properties such as distributing of natural balance, density, hydrogen bonding, and hydrophobicity to change. Also, tensile strain, tensile stress, and maximum load at breaking point in the treated cotton fabric are higher than the cotton fabric. Altering of crystallinity as shown in XRD patterns caused the modulus of the treated fabrics to be lower than the untreated cotton fabric. Prepared nano-emulsions have similar chemical structure of the cotton fabric and can cover weak points of fibers. Because of this, treated cotton fabric with nano-emulsions has more strength than the cotton fabric.

Conclusion

In this research, the preparation of ChD hybrid as an antibacterial agent for cotton fabric was reported. FTIR, SEM, and DSC results confirmed the reaction between chitosan and PAMAM dendrimer. Also, ChDN was prepared through ionic gelation with mean particle size of 265 nm, when concentration of TPP and ChD was 1 mg/m*l* and 2 mg/m*l*, respectively. Mean particle size of ChDN was increased by chelation with silver ions, and was a good sign of attachment of silver on the ChDN surface. The cotton fabric was treated with nano-emulsions. SEM and XRD results confirmed the presence of particles on the treated cotton

fabric surface. In addition, treated cotton fabrics with ChD and Ag-ChD nano-emulsions strongly had the antibacterial potential with high resistance against *E.coli*, and silver ions increased antibacterial activity of ChDN. *K/S* values of cotton fabric treated by nano-emulsions were the same as cotton fabric dyed with salt in concentration of 25 g/*l*. So, by this modification method, not only salt adding pollution was diminished, but dyeing efficiency of cotton fabric with reactive dyes was also enhanced. The color fastness and mechanical strength of treated fabrics were all good and can meet the need for use.

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